

Food and Agriculture Organization of the United Nations





MEDSUDMED - TECHNICAL DOCUMENTS

Report of the MedSudMed Oceanographic Survey: Libyan continental shelf -South central Mediterranean Sea (15 - 31 July 2008)



REPORT OF THE MEDSUDMED OCEANOGRAPHIC SURVEY: LIBYAN CONTINENTAL SHELF – SOUTH-CENTRAL MEDITERRANEAN SEA

(15 - 31 JULY 2008)

FOOD AND AGRICULTURE ORGANIZATION OF THE UNITED NATIONS Rome 2015

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Preface

The Regional Project "Assessment and Monitoring of the Fishery Resources and the Ecosystems in the Straits of Sicily" (MedSudMed) is executed by the Food and Agriculture Organization of the United Nations (FAO) and funded by the Italian Ministry of Agriculture, Food and Forestry Policies (MiPAAF). The Directorate-General for Maritime Affairs and Fisheries of the European Commission (DG MARE) co-funded the project since October 2012. The Italian Regione Siciliana funded a project aimed at strengthening MedSudMed's effectiveness on issues related to demersal resources, namely crustaceans, for 18 months, starting from May 2011.

MedSudMed promotes scientific cooperation between research institutions of the four participating countries (Italy, Libya, Malta and Tunisia), for the continuous and dynamic assessment and monitoring of the status of the fisheries resources and the ecosystems in this area of the Mediterranean Sea.

Research activities and training are supported to increase and use knowledge on fisheries ecology and ecosystems, and to create a regional network of expertise. Particular attention is given to the technical coordination of the research activities between the countries, which should contribute to the implementation of the FAO Code of Conduct for Responsible Fisheries and the Ecosystem Approach to Fisheries. Consideration is also given to the development of an appropriate tool for the management and processing of data related to fisheries and their ecosystems.

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Publications

The MedSudMed Project publications are issued as series of Technical Documents (GCP/RER/010/ITA/MSM-TD-00) and Scientific Reports (GCP/RER/010/ITA/MSM/SR-00) related to meetings, missions and research organized by or conducted within the framework of the Project.

Comments on this document would be welcomed and should be sent to the Project headquarters:

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Preparation of this document

Oceanographic surveys are probably the most important source of data to investigate the ecology, abundance and spatial distribution of small pelagic fish species, and to detect possible influence of environmental factors on their abundance and distribution. The experts of the countries participating in the FAO Project MedSudMed, during the "MedSudMed Expert Consultation on Small Pelagic Fish: Stock Identification and Oceanographic Processes Influencing their Abundance and Distribution (Tunisia, October 2003)", deemed necessary to expand the area covered by oceanographic surveys in the south-central Mediterranean Sea and investigate areas where little or outdated information on eggs and larvae was available.

This document is the final version of the report of the MedSudMed Oceanographic Survey carried out in Libyan waters from 15 to 31 July 2008 on board of the R/V Urania. The document presents the results of the processing of the data collected during the survey. The survey was organised in the framework of the MedSudMed Project in cooperation with the Istituto per l'Ambiente Marino Costiero (IAMC-CNR) of Mazara del Vallo (Italy) and the Marine Biology Research Centre (MBRC) of Tajura (Libya). Other collaborating research institutes involved in the survey and in the data processing are: i) ISMAR-CNR, Istituto di scienze marine, Sezione di Oceanografia Fisica, La Spezia, Italy; ii) Istituto Nazionale di Geofisica e Vulcanologia, La Spezia, Italy; and iii) IAMC – CNR of Messina, Italy. The outcomes of the survey and data processing described in this report contributed to the publication of MedSudMed identification sheets for early life sages of bony fish (MedSudMed Technical document No. 18¹ http://www.faomedsudmed.org/pdf/publications/TD18.pdf).

This report is one of results of the MedSudMed Project component on "Small Pelagic Fish: Stock Identification and Oceanographic Processes Influencing their abundance and distribution". This report is primarily for scientists of the south-central Mediterranean Sea; it can also be of interest for students and professional of fisheries research and management in the Mediterranean Sea region. It is believed to be a contribution to improve knowledge on the distribution and abundance of small pelagic fish and of some oceanographic parameters in an area not fully investigated.

¹ FAO MedSudMed 2011. Identification sheets of early life stages of bony fish. Western Libya, Summer 2006. GCP/RER/010/ITA/MSM-18 (MedSudMed Technical Documents n°18). 2011. 251pp.

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ABSTRACT

This document is the final version of the report of the MedSudMed Oceanographic Survey carried out in Libyan waters from 15 to 31 July 2008 on board of the R/U Urania. The document also presents the results of the processing of the data collected during the survey. The survey was carried out under the cooperative framework promoted by the FAO Project MedSudMed (Assessment and Monitoring of the Fishery Resources and the Ecosystems in the Straits of Sicily). The main objective of the survey was to collect information on areas of concentration of eggs and larvae of small pelagic fish species and on the mesoscale physical aspects characterizing the area. Advantage was taken of the survey to collect sediments and water samples to update and/or complement existing information on bottom types and study the chemical-physical properties of the water masses. The results were expected to supplement information gathered during the first MedSudMed survey (August 2006) and information available in other parts of the MedSudMed area. The main target species for the ichthyoplankton study were anchovy (Engraulis encrasicolus) and round sardine (Sardinella aurita). An overall description of the sampling scheme, of the area explored and of the methods adopted is provided. The distribution and abundance of eggs and larvae of E. encrasicolus and S. aurita in Libyan waters is described, as well as the composition and abundance of phytoplankton. The main oceanographic characteristics, including water mass circulation in the western Libyan waters are also illustrated. A description of the trophic status of the waters is also provided taking into account nutrients and suspended matter. A description of the content of trace elements and nutrients in the water column complete the information provided in this report.

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1 Introduction

The regional assessment of small pelagic fish stocks and the study of the spatial distribution of the different life stages in relation to environmental parameters are two of the research activities endorsed by the MedsudMed Coordination Committee. These activities are developed in the framework of the MedSudMed Project component "Small Pelagic Fish: Stock Identification and Oceanographic Processes Influencing their abundance and distribution".

The MedSudMed Project has put considerable effort into support for scientific cooperation, standardization of methods for sampling and processing data and to conduct activities on a regional scale. The Project also supported participating institutes in strengthening capacity in data and sample collection at sea, their processing and statistical analysis. Along these lines, the Project supported the organization of acoustic, oceanographic and ichtyoplankton surveys with cooperation between the Marine Biology Research Centre (MBRC) of Tajura, Libya and the Istituto per l'Ambiente Marino Costiero (IAMC-CNR) of Mazara del Vallo, Italy. The surveys were instrumental in collecting data in areas where little or outdated information on small pelagic fish abundance and distribution and driving oceanographic factors was available. Other Institutes participated in the survey as partners of the IAMC-CNR due to their expertise on specific topics. The oceanographic survey MedSudMed-08 was conducted on board the Italian R/V "Urania" from 15 to 31 July 2008 in the central part of the Libyan waters.

The main scope of the survey was to define the areas of major concentration of eggs and larvae of small pelagic fish species and relate them to the mesoscale physical structures characterizing the area. The results were expected to complement information available in the rest of the Libyan waters and MedSudMed area, where hypothesis were drawn on the transport and retention processes of small pelagic fish eggs. Considering the reproduction period of small pelagic fish in this area, the main target species were anchovy (*Engraulis encrasicolus*) and round sardinella (*Sardinella aurita*).

Besides the main scientific target of the survey, advantage was also taken to collect sediments and water samples to update and/or complement existing information on bottom types and study the chemical-physical properties of the water, such as concentration of nutrients in the water column and trace elements concentration in located spots (i.e. in front of the main cities of the study area). The survey also provided the occasion to carry out on-the-job training and reinforce cooperation relationships between the Institutes.

Prior to the survey, it was agreed that data and samples would be processed jointly by the different participating institutes and, whenever required, training courses would be organized in the laboratory. As a result, six training courses were organized in parallel to the data processing and to the preparation of the technical reports that were used as the basis for this document.

This document gives an overview of the work at sea and of the main findings related to ichtyoplankton, oceanography, sediments, phytoplankton, organic matters, nutrients, trace elements, meteorology.

2 Objectives and study area

The oceanographic survey MedSudMed-08 was conducted on board the Italian R/V "Urania" from 15th to 31st July 2008 in the central part of the Libyan waters (Gulf of Sirt) and was the second survey carried out in cooperation between CNR-IAMC and MBRC under the framework of the FAO MedSudMed Project component on "Small Pelagic Fish: Stock Identification and Oceanographic Processes Influencing their abundance and distribution". Other institutes participated in the survey in their capacity as partners of the CNR-IAMC.

Research activities mainly focused on eggs and larvae of small pelagic fish in part of the MedSudMed study area, in relation to biological and physical processes. Considering the reproduction period of small pelagic fish in this area, the main target species were anchovy and round sardinella. The study area is shown in Figure 1.

The main objectives of the survey were:

- delineation of the spawning areas of the target species;
- study of the correlation between mesoscale physical structures and the distribution and abundance of small pelagic fish eggs and larvae and zooplankton in the study area;
- measurement of physical parameters with a multiparametric probe;
- analysis of sediments.

The survey was organized with the aim of collecting data in the in the Gulf of Sirt, as a follow-up to the first survey that covered the western part of the Libyan waters. The overall objective was to get a regional representation of transport patterns of small pelagic fish eggs and larvae and to identify the oceanographic features that are responsible for retention areas.

The main study area of the MedSudMed-08 Oceanographic survey spans from parallels 30° and 33° and meridians 14° and 21° (Gulf of Sirt). Sampling was also carried out along a transect between Capo Passero (Sicily) and Misurata (Libya). The study area, including all the stations, is described in Figure 1 (CTD stations, LADCP and Bongo 40), Figure 2 (sediments, water, phytoplankton and zooplankton), Figure 3 (water samples for nutrient analysis, isotopes, trace metals, Particulate Organic Carbon [POC], Particulate Organic Nitrogen [PON]).

3 Participating Institutes and Scientific Staff

Scientists from the following research institutions participated in the organization and carrying out of the survey:

- 1. Istituto per l'Ambiente Marino Costiero (CNR-IAMC), Mazara del Vallo Section, Italy;
- 2. FAO MedSudMed Project;
- 3. Marine Biology Research Centre (MBRC), Tripoli, Libya;
- 4. Istituto di Scienze Marine (CNR- ISMAR) Oceanografia Fisica Section, La Spezia, Italy;
- 5. Istituto per l'Ambiente Marino Costiero (CNR-IAMC), Messina Section, Italy.

Role on Name Sex Citizenship Skills Title Institutions board **CNR-IAMC** 1) Angelo Researcher Chief scientist Μ Italian Oceanography Bonanno CNR Mazara (TP) 2) Sergio Interdisciplinary Misc. **CNR-IAMC** Researcher М Italian Bonomo measurements CNR measurements Mazara (TP) 3) Ignazio Interdisciplinary Collaborator Misc. **CNR-IAMC** Italian Μ Fontana measurements CNR measurements Mazara (TP) 4) Mireno Oceanographic Technician Misc. **ISMAR-CNR** Μ Italian Borghini measurements CNR measurements La Spezia 5) Salem Interdisciplinary Researcher Misc. MBRC Μ Libyan measurements MBRC measurements Tripoli Zgozi 6) Paola Interdisciplinary Researcher Misc. **CNR-IAMC** F Italian Rumolo measurements CNR measurements Napoli 7) Abdul Bari Interdisciplinary MBRC Researcher Misc. Libyan Μ Ramadan measurements MBRC measurements Tripoli 8) Daw Interdisciplinary Researcher Misc. MBRC Libyan М MBRC Haddoud measurements measurements Tripoli **CNR-IAMC** 9) Simona Interdisciplinary Researcher Misc. F Italian Genovese measurements CNR measurements Mazara (TP) 10) Adbul Interdisciplinary Researcher Misc. MBRC Μ Libyan Fatah measurements MBRC Tripoli measurements 11) Giovanni Interdisciplinary Collaborator Misc. **CNR-IAMC** Μ Italian Giacalone measurements CNR measurements Mazara (TP) 12) Akram Interdisciplinary Researcher Misc. MBRC Μ Libvan El Turki measurements MBRC measurements Tripoli 13) Massimo Interdisciplinary Collaborator Misc. **CNR-IAMC** М Italian De Luca measurements CNR measurements Mazara (TP) 14) Rossana Interdisciplinary Collaborator Misc. **CNR-IAMC** F Italian Borghi measurements CNR measurements Mazara (TP) 15) Mohamed Interdisciplinary Researcher Misc. MBRC Μ Libyan measurements Hamza MBRC measurements Tripoli 16) Interdisciplinary Collaborator **CNR-IAMC** Misc. Mariangela F Italian measurements CNR measurements Mazara (TP) Borghi 17) Umberto **CNR-IAMC** Interdisciplinary Misc. Μ Italian Collaborator Speziale measurements measurements Mazara (TP) 18) Adele Interdisciplinary Misc. **CNR-IAMC** F Collaborator Italian Bianco measurements measurements Mazara (TP) 19) Monica Interdisciplinary Technical **CNR-IAMC** Misc. F Italian Calabrò measurements collaborator measurements Mazara (TP) 20) Francesca Interdisciplinary Scientific Misc. **CNR-ISMAR** F Italian Polonelli measurements collaborator measurements La Spezia 21) Ali Kalefa Μ Libyan Coast Guard Observer Tripoli

Scientific Staff on board.

Work shifts					
1 st shift	2 nd shift	3 rd shift			
08:00 - 12:00	12:00 - 16:00	16:00 - 20:00			
20:00 - 24:00	24:00 - 04:00	04:00 - 08:00			
Angelo Bonanno	Massimo De Luca	Giovanni Giacalone			
Ignazio Fontana	Adele Bianco	Rossana Borghi			
Abdul-Bari Ramadan	Daw Haddoud	Mohamed Hamza			
Salem Zgozi	Abdul Fatah	Akram El Turki			
Mariangela Borghi	Umberto Speziale	Monica Calabrò			
ADCP Mireno Borghini; Francesca Polonelli					
Water samples Paola Rumolo, Simona Genovese, Sergio Bonomo					

The shifts on board were organized as follows:

3. Diary of the survey

1st day: Tuesday 15 July 2008 (Syracuse – Strait of Sicily)

The morning was dedicated to administrative formalities for the embarkation of the scientific crew and instruments. Notice was given that the relevant Libyan Authorities had released the requested authorizations to carry out the survey in the Libyan waters and it was therefore decided to leave right after completing the embarkation formalities. Work shifts were set. The vessel left Siracusa at 17.30 hours. Upon departure, the weather conditions were not optimal, but improved during the night. It was decided to start sampling along the transect between Capo Passero and Misurata. The following samples/data were collected for stations M1 and M2 (Table 1): sediments (box core), water (niskin bottles), CTD casts, current velocity profiles (ADCP).

2nd day: Wednesday 16 July 2008 (Strait of Sicily – Libyan waters)

The activities continued along the transect towards Misurata; the stations M3 to M10 were covered (Table 1). Moderately rough sea.

3rd day: Thursday 17 July 2008 (Misurata)

Moderately rough sea. At 02.00 hours completion of station M11. The vessel steered toward Misurata to embark the six MBRC scientists and the coast guard. During the CTD acquisition, spikes were recorded on the casts, probably because of the defective steel cable. During the morning, the cable was shortened by 20 m to solve the problem. The MBRC scientists and the coast guard got on board at 17.00 hours. A short meeting was held to discuss details of the sampling design and the duties of the staff. The vessel then steered toward the first station (L2821). During the evening, the stations M12, L2718, L2716 and L2713 were covered (Table 1).

4th day: Friday 18 July 2008 (Libyan waters, Misurata - Tawerga)

Sampling and acquisition activities were carried out all day and night according to the established sampling design. The weather and sea conditions were excellent. Stations L2813, L2816, L2819, L2920, L2918, L2915, L2912, L3013, L3016, L3019, L3022, and L3024 were covered. Coordinates of station L3138 were shifted to L3138M due to the presence of a wreck.

5th day: Saturday 19 July 2008 (Libyan waters, Tawerga – Bu'Ayrat al Hasun)

The weather conditions were good. The following stations were covered: L3136, L3133, L3130, L3250, L3253, L3256, L3258, L3260M, L3385M (position shifted because of shallow waters), L3383, L3380, L3377, L3374 and L3371. The list of the stations that were sampled during the day is reported in Table 1.

6th day: Sunday 20 July (Libyan waters, Bu'Ayrat al Hasun - Syrt)

Good weather conditions, no clouds, smooth sea. The design of the WP2 samples was changed on the basis of the activities to be performed and on time availability (Figure 2). During the day, 11 Bongo 40 samples were collected and round sardinella and anchovy larvae were finally found in some of them. Details of the stations covered (L3368, L3500, L3503, L3506, L3509, L3511, L3636, L3634, L3632, L3629 and L3626) are described in Table 1.

7th day: Monday 1 July 2008 (Syrt)

Station L3742 was reached at 00.15 hours and samples/data were collected with the Rosette and the Bongo 40. The box corer unfortunately had operating problems and, after the second trial, it was decided not to sample sediments in that station. Work was carried on along the transect toward Sirt. Good weather conditions with light waves in the afternoon. Station L3757 was shifted to L3757M because of shallow waters. Work was carried out regularly without particular problem in stations L3745, L3748, L3751, L3754, L3873, L3872, L3869, L3866, L3863, L3977 and L3980. Table 1 includes information on the stations covered during the day.

8th day: Tuesday 22 July 2008 (central area between Syrt and Ras Lanuf)

Weather conditions improved during the night. A CTD cast was recorded between stations L4097 and L4085 at a 270 m depth (new point named Lvena). Station L4097 was moved due to shallow waters at the position initially planned. Samples and data collection were carried out all day without interruption in stations L3983, L3986, L4097M, L4094, L4091, Lvena, L4088, L4085, L4197, L4200, L4203, L4205, L4316 and L4314. Table 1 includes information on the stations covered during the day.

9th day: Wednesday 23 July (Ras Lanuf)

The weather conditions deteriorated due to a storm in the Strait of Sicily. Consequently, the wind reached 30 knots; however, sea conditions allowed the work to continue safely and quite regularly, despite some difficulties. Stations L4311, L4398, L4418, L4421, Lvena2, L4424, L4427, L4429, L4543, L4540, L4537, L4655 and L4658 were covered (Table 1).

10th day: Thursday 24 July 2008 (Ras Lanuf – Marsa el Brega)

Good sea and weather conditions. A core barrel was used at station L4775 and a core of 3.7 m length was extracted. The following stations were covered: L4661, L4663M, L4786M (both shifted because they were originally placed between the signal buoys of oil terminals), L4784, L4781, L4778, L4775, L4899, L4902, L4905, L4908, L4911M and L5004M (the last two stations were shifted due to shallow waters).

11th day: Friday 25 July 2008 (Marsa El Brega – Zuetina)

Calm seas. Excellent weather and sea conditions. The sampling design was modified because of a wide area in which navigation was forbidden. It was decided to shift all stations that were initially included in the forbidden area and to follow a zigzag track (Figure 1). Some of the coastal stations were shifted as well due to shallow waters. During the day, the following stations were covered: L5001, L4998, L4995, L4992, L5058, L5061, L5064, L5067, L5114, L5111, L5108, L5105, L5055 and L4989M (Table 1).

12th day: Saturday 26 July 2008 (Zuetina – Benghazi)

Another day with calm sea. The coastal stations were covered in the morning and the offshore ones during the afternoon. The following stations were covered: L4986M, L5052, L5102M, L5050M, L4983, L4890M, L4981, L4887, L4884M, L4760, L4637, L4763M, L4640 and L4766M (Table 1 and Figure 1).

13th day: Sunday 27 July 2008 (Benghazi – Misurata)

Good weather conditions. The last four CTD stations in deep waters were covered during the day (Figure 1 and Table 1).

14th day: Monday 28 July 2008 (Misurata – Strait of Sicily)

The night and part of the day were dedicated to the transfer between stations L3736 and Misurata. The vessel reached the anchor area at 13.00 hours to wait for the disembarkation of the MBRC scientists and the samples collected. Once the procedure was completed, the vessel left in the direction of Favignana. The journey took the rest of the day. Excellent weather and sea conditions.

15th day: Tuesday 29 July 2008 (Strait of Sicily)

The whole day was dedicated to the transfer towards the station "Geostar" for the sampling in deep waters (ref. Prof. Lupton).

16th day: Wednesday 30 July 2008 (Favignana - Palermo)

Station "Geostar" was reached at 11.40 hours (38°54.95' N 013°18.00' E). Vertical casts of oceanographic variables and water samples were collected at regular depth intervals of 200 m. At the conclusion of the sampling, the vessel set bound for Palermo, with arrival at 20.00 hours.

17th day: Thursday 31 July 2008 (Palermo Harbor)

The day was dedicated to the disembarking the crew and instruments.

4. Sampling design of the Oceanographic survey MedSudMed-08

The sampling design of the surveys is shown in the following figures 1, 2 and 3. Since the Libyan-Italian research team adopted a multidisciplinary approach in carrying out the survey, all the research activities performed in the study area are described in three different figures.



Figure 1. Position of CTD (red circles), LADCP (blue circles) and Bongo 40 (black circles) stations covered during the MedSudMed-08 survey on board R/V Urania



Figure 2. Position of the stations where sediments (green circles), Phytoplankton-POC-PON-Nutrients (brown circles) and zooplankton (blue triangles) samples were collected. Zooplankton was collected with VP2 gear.



Figure 3. Position of the stations where water samples were collected for the analysis of nutrients (blue circles), isotopes (green squares), trace metals (blue squares), POC and PON (red squares).

5. Oceanography

From a hydrological point of view the offshore and inshore Libyan waters in the Gulf of Sirt (between $11.8^{\circ}E - 20^{\circ}E$ and $30.4^{\circ}N - 34^{\circ}N$) are poorly investigated and the main oceanographic features are not completely understood. In general the information available is scarce and even the most complete and updated database of all the hydrological data of the Mediterranean, the Medar/MEDATLAS II (Medar Group, 2002) shows, since the beginning of the century, significant lack of data in this region.

The thermohaline characteristics and the water mass circulation along the Libyan coast are, as mentioned, not completely understood and the small amount of information available only allows a rather rough description of the hydrological conditions of the area. Some vertical sections, made outside the continental shelf (Guibout, 1987), suggest that the region plays a marginal role in the context of East-West water mass exchange with a small amount of Atlantic water (AW) and a low level of saltier intermediate water (LIW). In the deep layer, between the LIW and the seabed a colder and denser layer is observed in both winter and summer.

The classic circulation patterns (Ovchinnikov 1966) indicate an anticyclonic (clockwise rotation) movement both for surface and deep water. From these patterns some information can be deduced about the AW dynamics along the African coast and particularly along the Libyan coast. In general, the Atlantic water moves from west to east along the continental slope, as confirmed by numerical simulations (Beranger *et al.*,2005). The model results agree with the circulation patterns that suggest a classical type of anticyclonic circulation away from the coast both in the surface layer and in the deep one.

The coast of Libya is quite smooth and the shape of the seabed along the edge of the escarpment is characterized by a wide continental shelf. In the Gulf of Sirt it reaches its maximum extension (about 80 km) and thins gradually westward before expanding again back to Tunisia.

5.1 Material and methods

The survey area is situated between Lat. 30°N and 36.5°N and Long. 14.5°E and 20°E (figs. 1, 2 and 3). The oceanographic measurements and water sampling were carried out in 12 stations (M1-M12) along a transect north-south between Sicily and the coast of Libya (Figure 1), and in 60 stations located in Libyan waters and distributed along 9 transects perpendicular to the coast in order to cover much of the Gulf of Sirt (Figure 1). In the Gulf of Sirt the hydrographic profiles covered the region from the very shallow water along the coast to about 1600 m depth along the continental slope. In all the hydrological stations, continuous vertical profiles of conductivity, temperature, pressure and dissolved oxygen were obtained from the surface to the bottom by means of a CTD-rosette system consisting of a CTD SBE 911 plus, and a General Oceanics rosette with 24 Niskin Bottles. The probes were calibrated before and after the cruise at the NURC (NATO Undersea Research Centre) in La Spezia, Italy.

Simultaneous vertical profiles of horizontal current have been acquired using a lowered ADCP system (LADCP WH Sentinel of RDI Instruments), in collaboration with scientists from the ISMAR-CNR of La Spezia (Italy). All data have been processed using SBE standard software for the hydrographic data, while currents are computed applying the LDEO processing software, developed by Visbeck (2002).

5.2 Results

Temperature and salinity profiles of the 56 hydrological stations on the Libyan shelf are shown (as scatter-plots) in figure 5.2.1. The temperature profiles single out a well developed thermocline at a mean depth of about 24 m, and a progressive decrease of temperature from about 28 °C at the surface to 13.6 °C near the bottom. The stations located in the northern part of the Sicily-Libya transect show different temperature profiles mainly in the upper water layer.



Figure 5.2.1. Temperature (a) and salinity (b) vertical profiles of the 72 hydrological stations. (c) the acquired profiles are shown on the θ S⁻¹ diagram.

The salinity profiles evidence the AW signature with a minimum (S_{min}) at about 50 m. The successive increase reaches its maximum (S_{max}) at about 220 m (LIW core). Going deeper, both temperature and salinity appear almost constant near the bottom, evidencing a homogeneous bottom layer. The horizontal map of the salinity minimum (S_{min}) in figure 5.2.2a evidences a westward intrusion of fresher water along the coast, with the core at about 50-60 m depth. Its presence is well defined on the western side, while it is not clearly evident moving eastward. The S_{min} distribution evidences several fragmented structures, suggesting the very complex circulation of the surface water in the Gulf of Sirt.

The salinity maximum (S_{max}), the signature of the LIW core, shows values ranging from 38.92 to 38.71 (Figure 5.2.1). The S_{max} is found below 200 m in the deep region, while along the continental shelf it is positioned at about 160-180 m. Its distribution appears more regular than that of S_{min} , even if some small structures may be observed, probably due to topographic effects. Salinity clearly decreases moving from east to west, confirming a prevalent westward spreading of the LIW.

The interpretation of water masses movements has been conducted using both the current measurements of the LADCP and the estimated geostrophic currents. In figures 5.2.2 the geostrophic currents in the upper water layer (10, 25, 50 and 75 m) are shown. The currents pattern in all the showed depths single out a cyclonic vortex in the eastern part of the Gulf. The pattern of AW is quite complex in the western side and some meanders are evident; higher current speed is linked to the minimum of salinity (core of AW) and is particularly evident at 75 m depth (Figure 5.2.2).



Figure 5.2.2. Dynamic height and geostrophic currents at 10 m, 25 m, 50 m and 75 m.

5.2.1 The transect between the Sicilian and the Libyan coasts

In figure 5.2.3 temperature, salinity, fluorescence and oxygen fields along the transect between the Sicilian and the Libyan coasts are shown. The salinity section highlights the signature of the AW in the upper layer (about 200 m thick). It is worth noting that the core of the Modified Atlantic Water (MAW), characterized by salinity values less than 37.8 Psu, is located in the northernmost half of the transect, close to Malta and the Sicilian coast.

The stations located on the Libyan shelf reveal, as mentioned above, the AW signature at about 75 m. The core of the LIW (maximum of salinity about 38.9 Psu) is positioned at a depth of about 330 m and is only evident in the central part of the transect, south of Malta. The temperature field singles out a clear stratification, with higher values in the southern side of the transect. The fluorescence field shows the maximum in the depth layer 86 - 106 m.



Figure 5.2.3. Temperature, salinity, fluorescence and oxygen fields along a north-south transect connecting the Sicilian and the Libyan coasts.



Figure 5.2.3. continued.

6. Nutrients

Nutrients are essential for the development of primary production. The two most important nutrients in the marine environment are nitrogen and phosphorus. The relationships between the two nutrients determine the biology of the planktonic organisms in the sea (Bethoux et al., 1998, Ribera d'Alcalà et al., 2003, Krom et al., 2004; Schroeder et al., 2010). For the majority of primary producers N must be "fixed" before being used. The bioavailable nitrogen species are nitrates, nitrites and ammonia. The uptake of nutrients from the biological community determines a distribution gradient in the water column with a heavy loss in the euphotic zone and an increase in deep waters, due to the sinking of the organic material and its further remineralization. Although the Mediterranean is a relatively oligotrophic basin, with the Eastern area more oligotrophic than the Western part, the N:P ratio in deep water is high ($\sim 28:1$) compared to the adjacent Atlantic Ocean (16:1). This is basically determined by very low concentrations of P in the basin that make it a P-limited system. There are different hypotheses to explain why the Mediterranean is a P-limited basin. Between these hypotheses there are: i) phosphate, but not nitrate, are preferentially removed from the Levantine Deep water (LDW) by Saharan dust absorption (Krom et al., 1991); ii) there is excess of N fixation in the basin (Bethoux et al., 1992, 1998) and, iii) system is enriched with matter flows coming from land (river discharge and aeolian material (deriving from the Sahara desert but also from the industrialized European continental area).

One of the objectives of the cruise was the investigation of the role of nutrients in the southern part of the Mediterranean and to identify possible terrestrial influence (e.g fluvial contributions, flows of aeolian material) on primary production by acquisition of unprecedented geochemical dataset in the area. Combining chemical and physical tracers we tried to assess nutrient budget and pathways in the area.

6.1 Material and methods

a) Study area

In order to define the key forcing in the Sicily Channel a sampling scheme was adopted in two contiguous areas characterized by different oceanographic, morphologic and geographic features (Annex 4 - Figure 6.1.1). The first area (transect), approximately 500 km-wide, extended from the Sicilian (Capo Passero) to the Libyan (Misurata) coast. 11 sampling stations were chosen in relation to the morphologic and hydrologic features of the area. In the second area (Gulf of Sirt), an area of approximately 75.000 km² close to the Sahara desert, a total of 17 stations were identified, representing the different hydro-morphologic characteristics of the whole gulf.

b) Samples collection

Samples for nutrients analysis were carefully collected directly from Niskin bottles into 60-ml sterile high-density polyethylene bottles previously cleaned with 1M HCl. Bottles were rinsed three times with their own volume of sample water and immediately frozen at -20°C. As contamination is of primary concern, these samples were not filtered, thus the results of analysis represent total organic nitrogen (TON) and total organic phosphorus (TOP). This is a common procedure for oligotrophic waters where the particulate pool is generally considered negligible (<10% of the total N and P pool), whereas risk of contamination or cell breakage during filtration is very high (Abell *et al.*,2000).

Dissolved organic matter is not analysed by a standard routine nutrient determination procedure. Consequently, for analysis, the organic material in the samples must be subjected to a decomposition procedure, and subsequent determinations of the inorganic components are required. The analysis result represents the total amount (organic and inorganic) of the respective nutrient (TDN and TDP). The nutrient organic concentration (TON and TOP) is calculated by subtracting the inorganic concentration (nitrate and nitrite or phosphate) from the total one (TDN and TDP):

[TON]=[TDN]-[DIN]; [DIN]=[NO3-+NO2-+NH4+].

As calculated here, TON also includes dissolved ammonium. Although a rapid cycling of ammonium in the surface layer of the oligotrophic sea is reported, the concentration of NH4+ in analyzed samples was anticipated to be higher than the detection limit (0.12μ mol) of the TDN. For this reason the contribution of this fraction to the TON measurements is considered.

c) Laboratory Analysis

The determination of inorganic-organic nutrients and total phosphorus-nitrogen in seawater were performed through the continuous flow system AutoAnalyzer III (Continuos Flow) Bran + Luebbe (Annex 4 - Figure 6.2.1).

Water samples are completely thawed about 4-12 hours before analysis at room temperature in air or in a water bath (at 40°C) and introduced to the Continuous Flow Analyzer (CFA). CFA uses a multichannel peristaltic pump to mix samples and chemical reagents in a continuously flowing stream to automate colorimetric analysis. By segmenting the sample stream with air bubbles this system reduces mixing of adjacent samples and enhances mixing of the reagents within the sample stream. The segmented stream passes through a system of glass coils where mixing and time delays are accomplished. The sample-reagent mixture reacts chemically to produce a colored compound whose light absorbance is approximately proportional to the concentration of nutrients in the sample. Finally the absorbance is measured by a flow-through colorimeter located at the end of the flow path. The procedures for determination of inorganic nutrients are based on manual methods suitably adapted for an automatic system. All methods are shortly outlined as follows:

<u>For the determination of nitrate + nitrite</u>, nitrate is reduced to nitrite by a copper-cadmium reductor column at pH of 8.0. The nitrite ion then reacts with sulfanilamide under acidic conditions to form a diazo compound. This compound then couples with N-1-naphthylethylenediamine dihydrochloride to form a reddish-purple azo dye and is read at 550 nm.

<u>The method for determination of (ortho) phosphate</u> is based on the colorimetric method in which a blue color is formed by reaction of phosphate, molybdate ion and antimony ion followed by a reduction with ascorbic acid at pH < 1. The reduced blue phosphor-molybdenum complex is read at 880 nm.

<u>The procedure for determination of soluble silicate</u> is based on the reduction of silico-molybdate in acidic solution to molybdenum blue by ascorbic acid; oxalic acid is introduced to the sample stream before the addition of ascorbic acid to minimize interference from phosphate. The complex is read at 820 nm.

<u>The procedure for determination of ammonia</u> uses the Berthelot reaction, in which a blue-green colored complex is formed and measured at 660 nm. A complexing agent is used to prevent the precipitation of calcium and magnesium hydroxides. Sodium nitroprusside is used to enhance the sensitivity of this method. Alternative reagents are given for reaction with salicylate and phenate.

For total phoshorous-nitrogen determination, small modifications were brought at the Bran+Luebbe methodology for on-line sample mineralization. Nitrogen and phoshorous compounds are oxidized with peroxodisulphate to nitrate and ortho-phosphate in a heating bath at 118°C. The determination of ortho-phosphate is then based on the colorimetric method in which a blue is formed by the reaction of phosphate and molybdate followed by reduction with ascorbic acid at an acid pH. The posphomolybdenum complex is read at 880 nm.

Quality control / Quality assurance (QC/QA) routinely employed within the laboratory

For all analytical determinations calibration standards are prepared using natural seawater of low nutrient content or artificial sea water as sample matrix. The NSW (or ASW) is used as a "base" for the analysis of sea water samples and is measured prior to each set of samples run. In the following Table 6.2.1 both detection limits and precision of the performed methods are reported.

6.3 Results

Results of nutrient analysis for both areas, transect and gulf of Sirte, are reported in Table 6.3.1 (Annex 4).

The chemical analyss highlights the presence of low nitrate concentrations in the surface layer (0-150 m). Particularly, in samples collected along the transect, nitrate concentrations are $<0.2 \mu$ mol fom 0 to 150 m increasing to about 4 µmol in the intermediate layer (between 150 m to 400 m) and at about 6 µmol in the transition layer (400 to 800 m). Only in the M4 station nitrate concentrations are $>1 \mu$ mol at 150 m. In the Gulf of Sirte, nitrate concentrations in the surface layer (0-150 m) are $<0.1 \mu$ mol, except at in four stations (L3013, L3368, L3377 and L3751) where nitrate concentrations are about 2 µmol at 150 m. Values of nitrate in intermedie (150 m to 400 m), transition (400-800 m) and deep (>800 m) layers in the Gulf are 3.82, 5.48 and 4.94 µmol, respectively.

Phosphate (PO₄) and silicates (Si(OH)₄) have a similar profile in the water column in both transect areas in the Gulf with mean concentrations of 0.02 and 0.70 μ mol in the euphotic zone (0 to 150 m), 0.1 and

3.5 μ mol the in intermediate layer (150 to 400 m), 0.2 and 6.5 μ mol and in the transition layer (150 to 400 m). Finally, in the deep stations of the Gulf (>800 m), concentrations of PO₄ and Si(OH)₄ average 0.2 and 7.1 μ mol, respectively.

Althought ammonium concentration (NH₄) is difficult to detecte, the results show coerent distribution along the water column; the lowest values are detected in surface layers and a positive trend at depth is observed. In particular, stations of the transect show ammonium concentrations in surface, intermediate and deep layers with averages of 0.6, 0.8 and 1 μ mol, respectively. At the same depth, values in the stations of the Gulf are 0.7, 0.6 and 0.8 μ mol. In the deep layer (>800m) of the gulf, the concentration of ammonium is 0.97 μ mol. Moreover, the ammonium concentration is higher in stations near the main cities than off-shore, probably due to anthropogenic inputs.

<u>Horizontal distribution patterns</u> of nitrate, fosfate, silicate and ammonium are shown in Figs. 6.3.2; 6.3.3; 6.3.4 and 6.3.5 (Annex 6). To evidence the comparison between the two areas studied, the distribution patters of nutrients are values are reported down to 400m.

<u>Vertical distribution</u> of nutrients are show in Figs. 6.3.6; 6.3.7; 6.3.8; 6.3.9 (Annex 6). Specific transects (from coast to off-shore) are selected to investigate on terrestrial influence on nutrient concentration.

6.4 Discussion

Our preliminary results reveal relatively high concentrations of nitrates (~6 μ mol/l) and phosphates (~0.2 μ mol/l) in the transition layer (between 400 and 800 m) in both the studied areas. At these depths, the salinity profile identified transition and deep water masses while the LIW (Levantine Intermedia Water) appears between 200 and 400 m. The mean concentration of silicates in the deep water ~6.5 μ mol/l, greater than the average concentration in the intermediate water (~3.5 μ mol/l). Highest values of ammonium are detected near the coast probably due to anthropogenic input. Average N:P ratio in deep water is ~28:1 as reported by Ribera d'Alcala *et al.* (2003). No significant differences were found between nutrient concentrations collected in the Gulf and in the transect, suggesting that the Saharan dust probably plays a secondary role in nutrient distribution along the water column.

7. Trace elements

Concentration and distribution of trace elements in seawater are affected by: i) external sources (atmospheric and fluvial inputs) ii) removal mechanisms due to biological "uptake" and, iii) organic and/or inorganic particulate absorption. For this reason, some of the trace metals show a distribution pattern similar to that of macro-nutrients in the water column. Although most trace elements (Fe, Zn, Cu, Ni, Co, Ag, Ge and Cd) are of primary interest, only a limited number of scientific papers are currently available on their distribution and chemistry in a dissolved state in the Mediterranean Sea (Spivack *et al.*, 1983; Van Geen *et al.*, 1991; Morley *et al.*, 1997; Elbaz-Poulichet *et al.*, 2001).

7.1 Materials and methods

During the survey, a total of 54 seawater samples were collected along the entire water column (two duplicates at about 10 different depths) in 5 stations (Figure 7.1.1- Annex 5)

In order to minimize contamination risks, all parts of the sampling apparatus (bottles, pipet tips, vacuum filtration system parts, etc.) were pre-conditioned in laboratory and stored in plastic bags. The cleaning procedure consists of a multi-step washing process to remove any source of metal contamination from the inside of the bottles. Equipment in polyethylene and Teflon was used to ensure that metals potentially adsorbed into the bottles would be removed by acid cleaning. Plastic bottles for seawater sampling were filled up with HNO₃ 10% and placed under the deck for 4 days at room temperature. After this time, bottles were rinsed 2-3 times with ultrapure water, air dried, and singularly stored in polyethylene bags until sampling. Moreover, polycarbonate membrane filters, for particulate collection, were pre-weighed (to five significant figures), and stored in petri dishes for transport.

a) *Sampling collection*

Twenty-four Niskin bottles, fixed on a rosette with CTD instrumentation, were used for TM sampling. Samples for trace metals were collected directly from Niskin bottles in 1L polyethylene pre-cleaned bottles and then filtered through 47 mm, 0.4 μ m pore size, polycarbonate membrane filters. For total dissolved trace metal analysis, samples were acidified to a pH~2 with suprapur HNO₃ and stored at room temperature. These samples, filtered and acidified, were returned to their original bottle contained within a plastic bag, while the polycarbonate membrane filters were kept at T= -20°C.

Determination of trace metals in seawater samples was carried out at the IAMC-CNR geochemistry laboratory of Naples, adopting G. Scelfo's methodology, with small modifications, as explained below. *b) Laboratory Analysis*

The preparation procedure comprised a sample preconcentration phase (from initial sample volume of 250ml to a final one of 3ml) and a liquid-liquid extraction phase by mean of APDC/DDDC with chelating agents and chloroform as extraction solvent. All water samples were treated under a class 100 laminar air-flow clean-bench to minimize contamination risks. Analysis were performed by ICP-MS for Cd, Co, Pb determinations and by ICP-AES for Mo, Cu, Ni, V determinations.

The results obtained are reported in Table7.1.1 (Annex 5)

7.2 Results

First results on distribution and concentration (nmol/l) patterns of dissolved trace metal (Ni, Cd, Cu, Pb, Co, V, Mo) in the water column are described below:

Molybdenum: molybdenum distribution at every sampling station along the water column is reported in Figure 7.2.1 (Annex 5). Surface water concentration varies from 38,74 to 125 nmol/l at stations M3 and M6, respectively, while in the deep waters, the concentrations range between 47,50 and 78,15 nmol/l (st. L4418).

<u>*Copper:*</u> chemical analyses carried out on the water samples revealed non-homogeneous copper distribution in the water column (Figure 7.2.2 –Annex 5). In particular, surface waters show a range of variability between 3,33 to 14,24 nmol/l in stations M9 and L4418 respectively, and 1 to 6,37 nmol/l in deep layers (st. L4418).

<u>Nickel</u>: nickel concentrations are characterized by high values (6,97 nmol/l) in the surface waters of stations M1 and M3 (Figure 7.2.3- Annex 5), whereas the highest concentrations are recorded in deep waters and are 10,57 nmol/l (st. M9).

<u>Vanadium</u>: Vanadium concentrations (Figure 7.2.4- Annex 5) in surface waters vary between 15,01 and 34,81 nmol/l at stations M3 and M6, respectively. Cconcentrations in deep waters range between 12,43 and 28,30 nmol/l at 900 and 600 meters, respectively (st. 4418).

<u>*Cobalt*</u>: The atypical behavior of the cobalt distribution is indicated in Figure 7.2.5- Annex 5, with high cobalt concentration in surface waters (1,06 nmol/l) of the M1 station. At M9 station, cobalt concentration at 700 and 800 m range between 0,02 and 1,27 nmol/l, respectively.

<u>*Cadmium*</u>: cadmium does not exhibit the typical nutrient-like distribution along the water column (Figure 7.2.6 – Annex 5). Results of chemical analysis highlight the presence of high concentrations in surface waters (from 0,06 to 0,3 nmol/l) in the stations M3 and M9with highest values measured in deeper waters (0,32 nmol/l at 700 m) (st. M9).

<u>Lead</u>: chemical analyses of Pb distribution in in seawater (Figure 7.2.7 – Annex 5), show the highest values in surface waters (0,29 - 2,07 nmol/l) at the stations M6 and M9 and a range of variability deep waters 0,8-4 nmol/l.

7.3 Discussion

Hereafter we reported a number of selected vertical sections drawn through key areas of the investigated system that are useful to get a wider view of both horizontal and vertical distribution patterns of the trace metals analysed. Basically, trace metal concentrations are higher in the whole area if compared to the seawater. In particular, concentrations of nickel (Figure 7.3.1 – Annex 5) are high both in the surface and deep waters, mainly near to the coasts (Sicilian and Libyan). Copper concentrations are high all along the water column near the Gulf of Sirte (Figure 7.3.2) and especially enriched in the LIW.

Cadmium shows high concentrations particularly in the Gulf of Sirt (Figure 7.3.3).

Lead concentrations are high both in the surface and deep waters near to the Gulf (Figure 7.3.4). Distribution of molybdenum and vanadium is consistent in the whole transect (Figure 7.3.5) with exception of the Sicilian coastal waters. These variations in different water masses are low throughout the transect.

Cobalt shows a distribution characterized by a high depletion in surface waters and increasing concentrations in the intermediate part of the water column, mainly in the Libyan area.

8. Particulate Organic Matter (POM)

Particulate Organic Matter (POM), which mainly consists of phytoplankton, microzooplankton and bacteria in the marine environment, plays an important role in cycling of bioavailable elements. POM is used to evaluate the trophic status of the waters. However, POM is important not only for the assessment of marine resource but also for the understanding of the marine carbon cycle. Due to its significant vertical transport, it enables the sea to remove carbon dioxide from the surface layer and carry it to the deeper parts of the sea or settle permanently as sediment on the sea floor. This study presents observations of Particulate Organic Carbon (POC) and Particulate Organic Nitrogen (PON) concentrations in the Gulf of Sirt and in the transect connecting Cape Passero (Sicily) and Misurata. The main aim was to collect new information about concentration and distribution of POC and PON in two areas considered extremely important for species composition.

8.1 Material and methods

a. Samples Collection

During the MedSudMed-08 survey, 63 water samples were collected in surface layers (0-150 m) of water column in 20 stations located in the Gulf of Sirt and in the transect connecting Cape Passero (Sicily) and Misurata (Figure 8.1.1). Samples of waters were collected with Niskin bottles for the analysis of POC (Particulate Organic Carbon) and PON (Particulate Organic Nitrogen) concentration. In the Gulf of Sirt sampling stations were chosen according to an nearly regular grid about 24 nautical miles in size; the sampling design was also adapted according to the time available, forbidden areas, etc. For TSM (Total Suspended Matter), POC (Particulate Organic Carbon) and PON (Particulate Organic Nitrogen) measurements, suitable quantities of water samples (1000 ml) were initially screened through a 200 μ m net to remove larger zooplankton and then filtered on precombusted (450 °C, 4^h) and preweighted Whatman GF/F filters (0.75 μ m pore size). After filtering, the samples collected on filters were dried (60 °C, 12^h) and stored at -20°C.

b. Sample Processing

In the laboratory the filters were weighted to calculate the TSM incidence. Subsequently, the filters were exposed to hydrochloric acid fumes for 6^{h} at room temperature (Iseki *et al.*, 1987), to destroy the inorganic carbon, then were dried (60 °C, 12^{h}) and rolled into tin discs. Finally POC and PON analyses were performed by a Perkin-Elmer CHN Elemental Analyser (Mod. 2400) at a combustion temperature of 980 °C, using Acetanilide as standard.

8.2 Results and discussions

The estimated values of TSM, POC and PON are reported in Table 8.1.1. Only samples in the upper 200 m are collected. Total Suspended Matter (TSM) values are in the range 4.7 mg/l – 9 mg/l; in the station L5067 the highest TSM value (13.65 mg/l) was estimated in the surface sample (0m). The POC and PON concentrations ranged between 8.47-146.87 μ g/l and 1.47-24.40 μ g/l, respectively. The highest POC values were recorded in the euphotic layer (max = 146.87 μ g/l at St. L3387). The POC and PON values were not particularly high, but higher than those we had found in our previous investigations in the Sicily Channel.

POC concentrations observed in the upper 100m at all stations followed a decreasing trend with depth (Figure 8.2.2) with lowest value a depth >100m. Opposite trend is observed for PON.

Despite being summer, no primary production is present, vertical POC distribution appear higher within 100m than over 100m. Correlation with Chla data are necessary for a better understanding.

The correlation between POC and PON is very good (Figure 8.2.3). The correlation coefficient (R^2) is better than 0.8. The average C/N atomic ratio of ~6.04 is very close to the Redfield ratio of 6.63. This agreement lends reliability to the analysis in this study. The clear relationship between POC and PON also provides a means to detect carbon contamination in the samples which may have resulted from the input of other sources of organic matter.

The C/N ratio values show a general balance between the trophic components (autotrophy, heterotrophy, detritus). In particular, a high level of efficiency of the autotrophic compartment was found in the eastern part of the study area, where mean C/N values ranged between 6 and 8. In the western part the mean C/N values, ranging between 4.6 and 5.9, indicate the prevalence of eterotrophic activities.



Figure 8.1.1 Position of stations where samples of water were collected for the POC, PON analysis (brown circles).



Figure 8.2.2. POC and PON profiles in the euphotic zone.



Figure 8.2.3. Correlation between Particulate Organic Carbon and Particulate Organic Nitrogen



Figure 8.1.3. Mean C/N ratio in the Gulf of Sirt.

Table 8.1.1. Estimated values of Total Suspended Matter (TSM), Particulate Organic Carbon (POC), Particulate Organic Nitrogen (PON) and C:N ratio

	Depth	TSM	POC	PON	C/N
Station	(m)	mg/l	μg/l	μg/l	
L 2718	0	6.853	62.13	10.93	5.68
	25	6.733	69.13	11.07	6.25
	100	6.073	85.60	15.20	5.63
L 3013	0	5.680	128.20	14.93	8.58
	25	8.000	64.07	10.07	6.36
	80	6.513	58.80	11.67	5.04
	100	7.593	24.20	5.87	4.13
L 3022	0	7.113	40.13	8.13	4.93
	25	6.807	74.67	14.93	5.00

	Depth	TSM	POC	PON	C/N
Station	(m)	mg/l	µg/l	µg/l	
L 3385M	0	6.280	41.47	7.87	5.27
	22	5.887	78.60	12.33	6.37
L 3377	0	6.360	33.60	6.27	5.36
	25	7.047	146.87	24.40	6.02
	100	6.753	118.53	21.87	5.42
L 3368	0	6.947	38.13	7.00	5.45
	25	6.947	66.60	11.27	5.91
	90	6.613	52.20	9.40	5.55
L 3742	0	7.560	66.60	10.67	6.24
	25	7.113	51.00	10.13	5.03
	100	7.047	50.73	8.93	5.68
	140	9.013	33.00	6.73	4.90
L 3751	0	6.273	73.00	13.67	5.34
	25	6.300	108.60	22.40	4.85
	120	6.853	43.60	9.80	4.45
L 4094	0	6.427	31.47	7.27	4.33
	25	6.553	62.87	12.07	5.21
	80	5.220	52.40	12.33	4.25
L 4085	0	6.533	17.27	4.87	3.55
	25	6.580	29.00	5.87	4.94
	100	7.173	29.40	5.00	5.88
	150	6.807	14.40	1.47	9.82
L 4418	0	6.753	57.40	8.93	6.43
	25	6.067	32.33	5.60	5.77
	100	6.207	17.93	4.00	4.48
	140	6.407	9.67	2.73	3.54
L 4427	0	4.907	23.93	3.87	6.19
	25	6.033	33.27	4.87	6.84
	50	5.807	48.53	6.13	7.91
L 4784	0	7.033	112.73	9.40	11.99
	25	6.680	58.07	8.80	6.60
	55	6.200	32.60	5.40	6.04

	Depth	TSM	POC	PON	C/N
Station	(m)	mg/l	μg/l	μg/l	
L 4775	0	6.460	16.00	1.87	8.57
	25	6.993	32.53	4.47	7.28
	100	7.587	8.47	2.47	3.43
	150	8.020	74.00	9.53	7.76
L 5105	0	6.860	48.20	7.67	6.29
	25	6.687	71.20	12.07	5.90
L 5067	0	13.653	58.07	9.27	6.27
	25	5.960	49.67	8.40	5.91
	43	5.773	83.60	13.07	6.40
L 4760	0	5.827	49.67	7.53	6.59
	25	7.133	24.07	4.27	5.64
	100	7.280	28.60	4.73	6.04
L 4766M	0	6.113	47.67	5.60	8.51
	25	6.787	43.40	6.00	7.23
	100	6.913	98.40	10.93	9.00
L 4412	0	7.227	51.20	7.27	7.05
	25	8.147	87.60	14.60	6.00
	100	5.013	22.13	3.47	6.38
	150	6.413	13.07	3.27	4.00
L 4079	0	6.540	98.33	17.60	5.59
	25	7.033	73.00	12.80	5.70
	100	4.700	72.47	9.27	7.82

9. Carbon and Nitrogen Isotopes of Particulate Organic Matter (POM)

The isotopic composition of particulate organic matter (POM) in the marine environment constitutes a tracer of surface biogeochemical processes, which may provide insight into physical, chemical and biological factors driving a magnitude of fluxes and composition of the particulate material which settle into deep water. Studies on particles flux and isotopic carbon and nitrogen composition of suspended and settling particulate organic matter, revealed a tight relation between surface and deep water biogeochemical dynamics (e.g. Altabet and Deuser, 1985; Voss *et al.*, 1996). However, in some cases, isotopic composition of suspended and settling POM did not interact due to the effects of other sources of organic material (inputs from coastal margin or atmosphere; e.g. Druffel *et al.*,1986). In order to determine the main sources of particulate organic matter along the water column in the Sicily Channel and in the Gulf of Sirte, and the influence of terrestrial inputs and Saharan dust on organic matter distribution, a first isotopic survey was carried out. In particular, the collected isotope data on POM in the two study sites provide a preliminary dataset useful for planning further studies on the biogeochemical dynamics of this area.

9.1 Material and methods

Sample of Particulate Organic Matter (POM) were collected in 10 stations. Twenty four bottles ("Niskin"), fitted on a rosette with CTD instrumentation, were used for POM sampling. Depth levels for sample collection were carefully selected by examining real-time CTD measurements. All water samples were filtered using the Dispensing Pressure Vessel (Millipore) through pre-combusted (450°C for 4h) GF/F filters (0,7 μ m pore size). This kind of filtration involved 5-8 l of water for each sample depending on the location and depth level of samples. At the end of the process, filters were put in Petri dishes, left for one hour at 60°C (without cover) and finally stored at –20°C.

Prior to analysis, filters were acidified with 1 mol HCl, dried at 60°C for 24h and stored in a dessiccator. Filters were then cut into 13 mm diameter disks, packed into tin capsules and loaded onto the EA autosampler. Duplicate analyses were performed for each sample. The isotopic compositions $\delta^{15}N$ and $\delta^{13}C$ were determined by a Thermo Electron Flash EA 1112 coupled to a Thermo Electron Delta Plus XP mass spectrometer tuned to carry out high sensitivity analyses.

Acetanilide (C_8H_9ON , Thermo Instruments) was used as standard for EA. Carbon and nitrogen calibration curves showed excellent linearity ($r^2=0.99$ and 0.99 for C_{org} and N_{tot} , respectively).

Sample sequences were run with blank cups and known urea standards. Standards were prepared by weighing from 0.5 to 2 mg of analytical grade urea (CH₄N₂O mw=60, C=20% N=46%) of certificated isotopic composition ($\delta^{13}C(\%)$ = -47,37 vs PDB and $\delta^{15}N(\%)$ = 0,02 vs AIR). Data quality control was checked by running the reference standard (urea) after each six samples.

Stable isotopes values were reported in ‰ delta notation:

$$\delta(\%_{00}) = \left[\frac{R_{sample}}{R_{reference}} - 1\right] (1000)$$

where δ (‰) stands for δ^{13} C (‰) or δ^{15} N (‰), and R_{sample} and R_{reference} are the isotopic ratios of sample and standard reference, respectively. Pee Dee Belemnite (PDB) and N air were used as reference standards for carbon and nitrogen isotopes.
9.2 Results

Values of δ^{15} N and δ^{13} C for suspended POM were measured in transect 4 and 6 in the Gulf of Sirt. Values of δ^{13} POC ranged from -28.61‰ to -21.83‰ while δ^{15} PON varied from -2.09‰ to 7.44‰ in both study areas.

In the stations M1, M3 and M6 similar trends of δ^{15} PON with depth were found, conversely, M6 station showed different responses with respect to M3 and M6 stations (Figure 9.2.1). The M9 station showed δ^{15} PON values increasing from 50 to 500m and a negative excursion at 800 m (Figure 9.2.2). Excluding the stations L4085 and L4418, the stations in the Gulf area also showed similar trends in δ^{15} PON as function of depth (Figure 9.2.3). The δ^{15} PON values are low at 50m and increase at ~100m. Below 100 m a small decrease in δ^{15} PON value can be observed but the station L3751 shows an evident increase at 200m and relatively stable values below.

In the stations of the transect (M1, M3, M6 and M9), values of δ^{15} PON at the surface (0-200 m) showed mean values of 0.93‰±0.64. It is worth noting that almost homogenous values occur between the stations with lowest values (e.g., M9 station with average 0‰) (Figure 9.2.4-a).

In the Gulf of Sirt (stations L3751, L5067, L4760, L3013, L4085 and L4418) δ^{15} PON values, integrated in the euphotic zone are less homogeneous than the transect values and show mean values of 1.11‰±1.5. However, excluding station L3013 characterized by high δ^{15} PON values at 80 and 150 m, the mean δ^{15} PON value drops to about 0.47‰±0.33 (Figure9.2.4-a). No comparison is made on samples deeper than 200 m, because few data were available for δ^{15} N-PON along the transect and Gulf stations, precluding a southeast-to-west comparison (Figure9.2.4-b).

We observed a significant southeast-to-west decrease in δ^{13} C-POC (<200m) (slope=-3*10⁻⁵-14.95; R²=0.5) (Figure 9.2.4-c). Samples deeper than 200 m present enriched δ^{13} C-POC values in the stations of the Gulf and depleted values in the M9 station of the transect.

The relationship between particulate δ^{13} C and δ^{15} N POM values is very weak, probably resulting from the dynamic water mixing. This lack of correlation could also indicate different biogeochemical pathways between carbon and nitrogen isotope fractions in the water column. However, if data points are considered relative to coastal stations (near cities), transect (open sea) and far from cities (middle stations in the gulf of Sirt), a weak correlation could be detected. The δ^{13} C and δ^{15} N of coastal stations ("near cities") are weakly and positively correlated, while heavier δ^{13} C and lighter δ^{15} N are met in the middle stations ("transect"). The average δ^{13} C POC value for coastal locations is around -24.7(±1.36)‰, while values for open sea locations and middle stations are around -25.23 (±1.5)‰ and -26.39 (±1.21)‰, respectively (Figure 9.2.5).

Terrestrial organic matter generally has an average δ^{13} C value from -26 to -28‰. A significant impact of terrestrial organic matter on δ^{13} C-POC values in the study area could explain the trends observed. The inner shelf water with a lower salinity could have received more terrestrial organic matter, source of lighter δ^{13} C POC values. Howerver, in some cases, the δ^{13} C values of POM from stations near the city are generally heavier than those from middle and far stations. Further investigation is needed to verify the primary forcing on PON sources.

The δ^{13} C and δ^{15} N profiles vs temperature in the transect stations and in the gulf stations, show an inverse trend. A positive correlation exists between δ^{13} C values and temperature. The lowest δ^{13} C values are observed in the same stations where the presence of a cold water mass is detected (Figure 9.2.6 a. and b.).

Finally, δ^{13} C values of POC show a general decrease with depth (Figure 9.2.7). Depleted values are detected in deeper stations of the Gulf, while in the transect a higher variability is present.

10. Phytoplankton

Phytoplankton is made up of minute organisms that are a key component of the oceanic ecosystem. Phytoplankton plays key roles in global biogeochemical cycles, particularly in the carbon-carbonate cycle (Honjo, 1976; Westbroek, 1991; Westbroek *et al.*, 1994), but also in the sulphur cycle since they produce dimethylsulphoniopropionate (DMSP), the precursor of dimethyl sulphide (DMS) (Keller *et al.*, 1989; Malin and Kirst, 1997) which may influence climate through stimulating cloud formation and influencing the Earth's radiative balance (Charlson *et al.*, 1987; Simó and Pedrós-Alió, 1999). Some algae are known to produce stable lipid compounds which can be used as a tool to evaluate paleoclimatic changes (Volkmen *et al.*, 1980; Brassell *et al.*, 1986). These properties, together with the fact that the ubiquitous species *Emiliania huxleyi* is a recognized bloom forming alga (Holligan *et al.*, 1993), confirm that the phytoplankton has an important role as an active biogeochemical and climatic agent.

Coccolithophores are unicellular planktonic algae belonging to the phylum Haptophyta, and have been one of the most important contributors to calcium carbonate production in the oceans since the Middle-Late Mesozoic. They are attracting growing attention in the light of their potentiality in evaluating the response of marine organism calcification to ocean acidification. Unlike any other plant in the ocean, coccolithophores surround themselves with a microscopic plating made of limestone (calcite). These scales, known as coccoliths, are shaped like hubcaps and are only three one-thousandths of a millimetre in diameter.

What coccoliths lack in size they make up in volume. A single coccolithophore is attached to or surrounded by at least 30 scales. Additional coccoliths are dumped into the water when the coccolithophores multiply asexually, die or simply make too many scales. In areas with trillions of coccolithophores, the waters will turn an opaque turquoise from the dense cloud of coccoliths. Scientists estimate that the organisms dump more than 1.5 million tons (1.4 billion kilograms) of calcite a year, making them the leading calcite producers in the ocean.

Most phytoplankton need both sunlight and nutrients from deep in the ocean. The ideal place for them is on the surface of the ocean in an area where plenty of cooler, nutrient-carrying water is upwelling from below. In contrast, the coccolithophores prefer to live on the surface in still, nutrient-poor water at mild temperatures.

Coccolithophores do not compete well with other phytoplankton. Yet, unlike their cousins, coccolithophores do not need a constant influx of fresh food to live. They often thrive in areas where their competitors are starving. Typically, once they are in a region, they dominate and become more than 90 percent of the phytoplankton in the area. Coccolithophores live mostly in subpolar regions. Some other places where blooms occur regularly are the northern coast of Australia and the waters surrounding Iceland. In the past years, large blooms of coccolithophores have covered areas of the Bering Sea. This surprises many scientists since the Bering Sea is normally a nutrient-rich body of water.

Coccoliths are not normally harmful to other marine life in the ocean. The nutrient-poor conditions that allow the coccolithophores to exist will often kill off much of the larger phytoplankton. Many of the smaller fish and zooplankton that eat normal phytoplankton also feast on the coccolithophores. In nutrient-poor areas where other phytoplankton are scarce, the coccolithophores are a welcome source of nutrition.

In the long term, the plants seem to be good for the environment. Coccolithophores make their coccoliths out of one part carbon, one part calcium and three parts oxygen (CaCO₃). So each time a molecule of coccolith is made, one less carbon atom is allowed to roam freely in the world to form greenhouse gases and contribute to global warming. Three hundred twenty pounds of carbon go into

every ton of coccoliths produced. All of this material sinks harmlessly to the bottom of the ocean to form sediment.

The coccolithophores' short-term effect on the environment is somewhat more complex. This effect again has to do with the formation of their coccoliths and the chemical reaction involved in the process. The chemical reaction that makes the coccolith also generates a carbon dioxide molecule, a potent greenhouse gas, from the oxygen and carbon already in the ocean. While much of the gas is sucked back in by the coccoliths (all plants take in carbon dioxide for food) some of it escapes into the atmosphere and immediately becomes part of the greenhouse gas problem. Scientists are concerned in the short term that greenhouse gases will cause the upper layers of the ocean to become more temperate and stagnant. This would increase the number of coccoliths in the world, which would produce more greenhouse gas. The coccolithophores also affect the global climate in the short term by increasing the oceans' albedo. Albedo is the fraction of sunlight an object reflects-higher albedo values indicate more reflected light. Coccolithophore blooms reflect nearly all the visible light that hits them. Since most of this light is being reflected, less of it is being absorbed by the ocean and stored as heat.

Diatoms are photosynthesising algae, they have a siliceous skeleton (frustule) and are found in almost every aquatic environment including fresh and marine waters, soils, in fact almost anywhere moist. They are non-motile, or capable of only limited movement along a substrate by secretion of mucilaginous material along a slit-like groove or channel called a raphe. Being autotrophic they are restricted to the photic zone (water depths down to about 200m depending on clarity). Both benthic and planktic forms exist. Diatoms are formally classified as belonging to the Division Chrysophyta, Class Bacillariophyceae. The Chrysophyta are algae which form endoplasmic cysts, store oils rather than starch, possess a bipartite cell wall and secrete silica at some stage of their life cycle. Diatoms are commonly between 20-200 microns in diameter or length, although sometimes they can be up to 2 millimetres long. The cell may be solitary or colonial (attached by mucous filaments or by bands into long chains). Diatoms may occur in such large numbers and be well preserved enough to form sediments composed almost entirely of diatom frustules (diatomites), these deposits are of economic benefit being used in filters, paints, toothpaste and many other applications.

Diatoms are divided into two Orders. The Centrales (now called the Biddulphiales) which have valve striae arranged basically in relation to a point, an annulus or a central areola and tend to appear radially symmetrical, and the Pennales (now called Bacillariales) which have valve striae arranged in relation to a line and tend to appear bilaterally symmetrical. The valve face of the diatom frustule is ornamented with pores (areolae), processes, spines, hyaline areas and other distinguishing features. It is these skeletal features which are used to classify and describe diatoms, which is an advantage in terms of palaeontology since the same features are used to define extant species as extinct ones. The classification system developed by Simonsen (1979) and further developed by Round *et al.* (1990) is currently the most commonly accepted. Diatoms commonly found in the marine plankton may be divided into the centric diatoms including three sub-orders based primarily on the shape of the cells, the polarity and the arrangement of the processes. These are the Coscinodiscineae, with a marginal ring of processes and unipolar symmetry, and the Biddulphiineae with no marginal ring of processes are bilded into two sub-orders, the Fragilariineae which do not possess a raphe (araphid) and the Bacillariineae which possess a raphe.

Diatoms have been well studied both in their natural habitat and in cultures by biologists and there is therefore a wealth of knowledge on their biology and ecology. The protoplast of diatoms consists of a cytoplasmic layer that lines the interior of the frustule and surrounds a large central vacuole, within the cytoplasmic layer there is a diploid nucleus and two to several pigment-bearing plastids (the site of photosyntheseis). The diatom frustule is often likened to a pill-box or agar dish with an epitheca (larger upper valve), and a hypotheca (smaller lower valve). The vertical lip or rim of the epitheca is called the epicingulum, and the epicingulum fits over (slightly overlaps) the hypocingulum of the hypotheca. The epicingulum and hypocingulum with one or several connective bands make up the girdle. Many diatoms are heterovalvate, i.e., the two valves of the frustule are dissimilar. This is most obvious within the family Achnanthaceae where one valve has a raphe and the other does not, and the Cymatosiraceae where one valve has a tubular process and the other does not. Chain-forming species with cells linked together by siliceous structures may, in addition, have separation valves. These valves are morphologically different from the valves within the chain. Therefore, one species may have four morphologically distinct types of valves.

Dinoflagellates are microscopic, unicellular, flagellated, often photosynthetic protists, commonly regarded as "algae" (Division Dinoflagellata). They are characterized by a transverse flagellum that encircles the body (often in a groove known as the cingulum) and a longitudinal flagellum oriented perpendicular to the transverse flagellum. This imparts a distinctive spiral to their swimming motion. Both flagella are inserted at the same point in the cell wall, by convention defining the ventral surface. This point is usually slightly depressed, and is termed the sulcus. In heterotrophic dinoflagellates this is the point where a conical feeding structure, the peduncle, is projected in order to consume food. Dinoflagellates possess a unique nuclear structure at some stage of their life cycle a dinokaryotic nucleus (as opposed to eukaryotic or prokaryotic), in which the chromosomes are condensed. The cell wall of many dinoflagellates is divided into plates of cellulose ("armor") within amphiesmal vesicles, known as a theca. These plates form a distinctive geometry/topology known as tabulation, which is the main means for classification.

Both heterotrophic and autotrophic dinoflagellates form a significant part of primary planktonic production in both oceans and lakes. Most dinoflagellates go through moderately complex life cycles involving several steps, both sexual and asexual, motile and non-motile. Some species form cysts composed of sporopollenin (an organic polymer), and preserve as fossils in the sedimentary record. Often the tabulation of the cell wall is somehow expressed in the shape and/or ornamentation of the cyst. Besides being important primary producers, and therefore an important part of the food chain, dinoflagellates are also known for producing nasty toxins, particularly when they occur in large numbers, called "red tides" because the cells are so abundant they make the water change colour. Besides being bad for a large range of marine life, red tides can also introduce non-fatal or fatal amounts of toxins into animals (particularly shellfish) that may be eaten by humans, who are also affected by the toxins. Many of these toxins are quite potent, and if not fatal, can still cause neurological and all sorts of other nasty effects. Add this to the rather ominous suspicion that red tides may be more common thanks to human inputs of phosphates and warmer global temperatures.

Silicoflagellates are a small group of unicellular heterokont algae, found in marine environments. At one stage of their life cycle they produce a siliceous skeleton, composed of a network of bars and spikes arranged to form an internal basket. These form a small component of marine sediments, and are known as microfossils from as far back as the early Cretaceous. There is one living genus, *Dictyocha*, with two commonly recognized species. There are also several extinct genera, but their classification is difficult, since skeletons may show diverse forms within each living species. *Dictyocha* has one golden-brown chloroplast and a long flagellum extended into a wing-like shape. The skeleton-bearing stage is uninucleate, with many microtubule-supported projections, and there are also uninucleate and micronucleate stages that do not produce skeletons, but how they relate to each other is poorly understood. The cell structure places the silicoflagellates in a group called the axodines. They are usually treated as an order, called the Dictyochales by botanists and the Silicoflagellida by zoologists.

The silicoflagellates, like the diatoms, are especially abundant in areas of upwelling and in equatorial waters but are also abundant at high latitudes. Silicoflagellates skeletons usually comprise 1-2% of the

siliceous component of marine sediments; they are thus much less abundant than diatoms. However, they are widely distributed throughout the world's oceans.

The quantitative analysis focuses on Coccolitophyceae species, hence supplementing previous work carried out at MBRC on diatoms, silicoflagellates and dinoflagellates (Tufail, 1981). Coccolithophyceae should be identified at level of genera and species. The expected outputs are:

i) the production of an atlas to documents the morphology, taxonomy and diversity of Coccolitophyceae in the Gulf of Sirte inspired by the publication dealing with NW Spain (Cros and Fortuño, 2002); ii) assessment of abundance (by species and total abundance) and comparison with abundance of eggs and larvae and possibly nutrients.

10.1 Material and methods

Samples of waters were collected with Niskin bottles in selected stations for the analysis of calcareous phytoplankton (Coccolitophyceae). Stations were chosen along transects perpendicular to the coast, the sampling design was then adapted according to the time available, forbidden areas etc. About 2 litres of sea water were filtered, using a vacuum pump, onto polycarbonate Nucleopore filters of 0.2 μ m pore size and 47 mm diameter. Each filter membrane was rinsed with distilled water immediately after filtration in order to remove all traces of sea salt. All membranes were stored in plastic Petri dishes, until preparation for the Polarized Microscope, and dried in an oven at 40 – 60 °C for several hours.

To investigate the total thickness of the photic zone we have selected these depth intervals: 0, -25, -50, -75, -100, -150 and -200 meters. A total of 105 samples were collected in 23 stations (Figure10.1.1).

For light microscope analyses a piece of filter membrane cut along its radius was mounted onto a glass slide using Norland Optical Adhesive and fixed beneath a cover slip. A similar sized piece of filter membrane was mounted onto an aluminium stub using carbon tape and coated with 15 nm of gold for subsequent analysis in the SEM. Cell counts were carried out with a Leica DM2500 polarizing light microscope (LM) using 100X objectives. The area represented by one field of view is 0.04521 mm². Calculation of the observed filtration area relies on the positioning accuracy of the stage and the accuracy with which the area of one field of view can be calculated. The area of observation is the sum of the area of all single fields of view. This is easily estimated and controlled with LM. It is important that single fields of view do not overlap to prevent double counting of specimens.

The number of coccolithophore cells in 1 l of water was calculated using the following equation:

$$CD = \frac{A * N}{a * v}$$

where CD= cell density (cells/l water); A= filtration area; N= total number of cells counted; a = analysed area; and v= volume of water filtered.



Figure 10.1.1. Sketch map of the investigated area.

10.2 Results

The results of quantitative analyses point out that, in the summer period, the phytoplankton association (Figs. 10.2.1, 10.2.2 and 10.2.3) of Gulf of Sirt is generally characterized by abundant Coccolithophyceae, followed by Diatoms and Dinoflagellates and rare to very rare Silicoflagellates.



Figure 10.2.1. Quantitative distribution surface map of analyzed Phytoplankton.



Figure 10.2.2. Quantitative distribution section (offshore and near coast) of analyzed Phytoplankton.



Figure 10.2.3. Scatterplot of analyzed Phytoplankton vs. Depth.

A generally negative trend in the primary production compound from East to West is recognizable.

<u>Coccolithophores</u>: water samples collected in this cruise confirm that coccolithophore production in the Mediterranean Sea is seasonally controlled (Knappertsbusch, 1993). In summer, the productivity is at least one order of magnitude lower and the occurrence of a seasonal thermocline leads to the development of a vertical zonation. Lower photic zone species can still profit from a rising nutrient flux at the base of the thermocline, while a typical K-strategist community grows in the surface waters of the mixed layer.

Identified Coccolithophores are shown in Table10.1. All recognized taxa have been grouped on the basis of coccosphere functional morphology (Table 10.2) which might reflect different ecological adaptations, following Young (1994). Placoliths (Figures 10.2.4, 10.2.5, 10.2.6), and *E. huxleyi* in particular, are overwhelmingly dominant in the areas of maximum standing stock. This group is formed by r-strategist taxa which rapidly exploit the nutrient uptake and, as observed in areas of upwelling (Okada and Honjo, 1973; Roth and Coulbourne, 1982), can be considered as a proxy of high productivity conditions (Young, 1994; Broerse *et al.*, 2000; Flores *et al.*, 2000; De Bernardi *et al.*, 2005; López-Otálvaro *et al.*, 2008). This consideration is also supported by a decrease in both absolute and relative abundances in the investigated area where a stable stratification stopped the nutrient flux and determined the minimum standing stock.



Figure 10.2.4. Quantitative distribution surface map of Placoliths group.



Figure 10.2.1. Quantitative distribution section (offshore and near coast) of Placoliths group.



Figure 10.2.2. Scatterplot of Placoliths group vs. Depth.

On the contrary, taxa grouped in the Upper Photic Zone (UPZ) group are K-strategists, specialized to live in warm subtropical surface waters and to exploit a minimum amount of nutrients (Okada and Mcintyre, 1979; Roth and Coulbourne, 1982; Takahashi and Okada, 2000; Andruleit *et al.*, 2003; Boeckel and Baumann, 2004; Baumann *et al.*, 2005). Coherently with this ecological niche, UPZ taxa have been found abundant in the upper part (-50 / -75 m depth) of the water column (Figure 10.2.7–10.2.8–10.2.9).

The patchy distribution of the Lower Photic Zone (LPZ) group (Figure10.2.10–10.2.11–10.2.12) (and its most important species, *Florisphaera profunda*) and of the Miscellaneous group (Figure10.2.13–10.2.14–10.2.15) which, as will be seen in the investigated area, assume great importance in the water column composition. Possibly, as further pointed out by other studies, coccolithophores in the lower photic zone, and mostly *F. profunda*, bloom following a complex interplay of environmental factors and their survey would require longer time series (Malinverno *et al.*, 2003; Dimiza *et al.*, 2008).



Figure 10.2.3. Quantitative distribution surface map of Upper Photic Zone group.



Figure 10.2.4. Quantitative distribution section (offshore and near coast) of Upper Photic Zone group.



Figure 10.2.5. Scatterplot of Upper Photic Zone group vs. Depth.



Figure 10.2.6. Quantitative distribution surface map of Lower Photic Zone group.



Figure 10.2.7. Quantitative distribution section (offshore and near coast) of Lower Photic Zone group.



Figure 10.2.8. Scatterplot of Lower Photic Zone group vs. Depth.



Figure 10.2.9. Quantitative distribution surface map of Miscellaneous group.



Figure 10.2.10. Quantitative distribution section (offshore and near coast) of Miscellaneous group.



Figure 10.2.11. Scatterplot of Miscellaneous group vs Depth.

One of the most interesting results is the distribution of *Gephyrocapsa oceanica*. This species seems to be confined to the offshore area and displays a good correspondence with the salinity minimum of the MAW flux. Such a consideration opened intriguing scenarios on the use of this taxon as a paleoceanographic proxy for surface waters of Atlantic origin and for evaluating possible incursions of this water mass into the eastern basin.

Finally, all data collected indicate that, like at mid-latitude oceans, coccolithophore develop a vertical zonation, with K-strategists taxa in the uppermost part of the water column and lower photic zone taxa below the seasonal thermocline.

<u>Diatoms</u>: quantitative distribution show high abundance values in the first 100 - 150 meters in the off shore of the investigated area. Near shore a less abundant concentration, mainly in the easternmost part of investigated Gulf, can be recognized. In generally diatoms are a common phytoplankton compound of the Libya eastern coast (Figures 10.2.16, 10.2.17, 10.2.18).



Figure 10.2.12. Quantitative distribution surface map of Diatom association.



Figure 10.2.13. Quantitative distribution section (offshore and near coast) of Diatom association.



Figure 10.2.14. Scatterplot of Diatom association vs. Depth.

<u>Dinoflagellates</u>: in the investigated area. Dinoflagellate quantitative distribution show high density values in the summer period in the first 25 - 50 meters of the water column, mainly in the stations near shore. A clear reduction of the abundances is evidently noticeable in offshore areas (Figures 10.2.19, 10.2.20, 10.2.21).



Figure 10.2.19. Quantitative distribution surface map of Dinoflagellate association.



Figure 10.2.20. Quantitative distribution section (offshore and near coast) of Dinoflagellate association.



Figure 10.2.21. Scatterplot of Dinoflagellate association vs. Depth.

<u>Silicoflagellates</u>: the Silicoflagellates of the Gulf of Sirt, as expected, showed very low values and were confined to the deeper central zone. The recognized assemblage is constituted only by *Dictyocha fibula* specimens that never go above 150 cell/l density.

Table 10.1 Coccolithophores identified from samples collected during the MedSudMed-08 Oceanographic Survey along the Libyan Continental shelf

Coccolitophyceae species
Algilosphaera spp.
Braarudosphaera begelowii
Calcidiscus leptoporus
Calciopappus rigidus
Calciopappus spp.
Calciosolenia spp.
Calciosolenia murray
Ceratolithus spp.
Ceratolithus cristatus
Coronosphaera mediterranea
Coronosphaera spp.
Cricosphaera spp.
Cristallolithus hyalinus
Discosphaera tubifera
Emiliania huxleyi
Ericiolus spp.
Florisphaera profunda
Gephirocapsa oceanica
Gephyrocapsa spp.
Gladiolithus flabellatus
Gladiolithus spp.
Helicosphaera carteri
Helicosphaera pavimentum
Helicosphaera spp.
Holodiscolithus
Oolithotus fragilis
Pontosphaera spp.
Rhabdosphaera clavigera
Rhabdosphaera spp.
Scyphosphaera apsteinii
Scyphosphaera spp.
Siracosphaera histrica
Siracosphaera pulchra
Siracosphaera spp.
Small placoliths
Umbellosphaera tenuis
Umbellosphaera irregularis
Umbellosphaera spp.
Umbilicosphaera sibogae
Umbilicosphaera spp.

Table 10.2 taxa recognized from samples collected during the MedSudMed-08 Oceanographic Survey along the Libyan Continental shelf grouped on the basis of coccosphere functional morphology

Groups	Taxa	Ecological preference
Placoliths	E. huxleyi, G. oceanica, small gephyrocapsids, Gephyrocapsa spp.	r-strategists, they exploit the nutrient flux quickly, proxies of high productivity.
UPZ	 A. quattrospina, R. clavigera, U. tenuis, U. sibogae, S. pulchra, A. brasilensis, holococcolithophorid, C. cristatus, T. heimii, D. tubifera, O. fragilis 	K-strategists, they live in warm and oligotrophic surface waters above a deep summer thermocline.
LPZ	F. profunda, T. flabellata, S. anthos	They live in the deep photic zone, within or below the summer thermocline.
Miscellaneous	 H. carteri, C. leptoporus, S. mollischii, S. lamina, C. multipora, C. oblonga, A. unicornis, M. splendens, P. apsteinii, Syracosphaera sp, B. bigelowii, S. catilliferus, H. pavimentum, C. mediterranea, others, A. robusta, H. triarcha, P. vandeli, P. syracusana 	They live without depth preference and within a wide range of ecological preferences. On the whole, they can be considered as weak K-strategists.

11. Ichtyoplankton

The Ichthyology of the Libyan waters was investigated very little in the past. The information is rather general, referring mainly to the whole Mediterranean, or giving statistical data about landings without special reference to species composition.

11.1 Material and method

a. Sample Collection

Biological samples were collected by means a Bongo40 net (Figure 11.1.1) with a 200 μ m mesh size for both sizes of the frame. Flow meters were used in each net (General Oceanic's, mod. 2030R). A depressor was used during the net hauling to enhance the stability of the nets. The lowering speed of the net was 0.75 m/s and the ascending speed 0.33 m/s. The Bongo40 net hauls described an oblique trajectory from the surface to 100m depth or to the bottom in areas where depth was less than 100m, at a constant speed of 2 knots with a cable inclination of about 45 degrees. 124 samples were collected, using a regular sampling grid of 12 nm.



Figure 11.1.1. Bongo40 during sampling operation

Samples were fixed immediately after collection and preserved in a 4% buffered formaldehyde seawater solution; the individual larvae were conserved in liquid nitrogen.

b. Samples Processing

Ichthyoplankton composition was estimated on samples coming from one of the two mouths of the Bongo40 net. Zooplankton biomass values are expressed as Wet Weight (W.W.) and Dry Weight (D.W.) (mg/m), according to Lovegrove (1966).

11.2 Results

Some details on the species composition (results of sorting) are reported in Table 11.2.1. Anchovy larvae (2.9 %) and round Sardinella larvae (1.6 %) are not the predominant species. Each of the other species represents only a minor fraction of the collected larvae, except the genus Vinciguerria (16.3 %), *Cyclothone braueri* (14.3%), the Gobidae family (9.5 %) and the Labridae family (6.9 %).

Seeanographic Sarvey along the Libyan Continental sher									
	Number of Number of		% of	Number of	% of	Other	% of	Total	
	Bongo40	Anchovy	Anchovy	Sardinella	Sardinella	larvae	Other	number	
	stations	larvae	larvae	larvae	larvae		larvae	of larvae	
GSA 21 (Gulf of Sirte- Libya)	124	54	2.9	31	1.6	1801	95.5	1886	

Table 11.2.1. Number and Percentage of larvae collected during the MedSudMed-08 Oceanographic Survey along the Libyan Continental shelf

Among the larval specimens collected in the Libyan waters 11 Orders, 32 Families, 38 Genera and 39 Species were identified (Table 11.2.2).

Table 11.2.2. Larvae collected during the MedSudMed-08 Oceanographic Survey along the Libyan Continental shelf.

MURENIDAE	Hygophum benoiti	LABRIDAE
Murena helena	Lampanyctus crocodilus	Gymnammodytes cicerelus
Echelus myrus	Lampanyctus pusillus	
Conger conger	Myctophum punctatum	BLENNIDAE
Ariosoma balearicum		Callyonymus maculatus
	MYCTOPHIDAE	
CLUPEIDAE	GADIDAE	GOBIDAE
Sardinella aurita	Ophildion barbatus	
Engraulis encrasicolus	Parophidion vassali	TUNNIDAE
Cyclothone braueri	Macroramphosus scolopax	
Vinciguerria attenuata	Scorpaena scrofa	SCOMBRIDAE
Vinciguerria nimbaria		Auxis rochei
Vinciguerria powerii	TRIGLIDAE	
	Ephinphelus alexandriunus	CENTRACANTHIDAE
VINCIGUERRIA		Lepidorhombus boscii
Synodus saurus	SERRANIDAE	
Lestidiops jayakari pseudosphyraenoides	Trachurus spp.	ARNOGLOSSUS
Paralepis affinis		Botus podas
Paralepis coregonoides	CARANGIDAE	
	Brama brama	BOTHIDAE
PARALEPIDAE	Pagrus pagrus	
Ceratoscopelus maderensis	Lythognatus mormirius	SOLEIDAE
Lobianca dofleny		Stomis boa
Diaphus holti	SPARIDAE	Zooplankton wt.
Electrona rissoil	Cepola macrophtalma	
	Chromis chromis	
	Coris julis	

The distribution map of of egg density for *Engraulis encrasicolus* found during the survey is provided in Figure 11.2.1. Figure 11.2.2 shows the distribution map of the non-identified larvae. The number of larvae for the main species collected during the survey is reported in table 11.2.3.



Figure 11.2.1. Engraulis encrasicolus egg density; range 0 – 0.111 eggs/m³.



Figure 11.2.2. Number of non-identified larvae (from 1 to 20 specimens)

Larvae	Total	%
Electrona risso	45	42.18
Lampanyctus pusillus	46	40.95
<u>Clupeidae</u> spp.	30	40.08
Gobiidae	179	39.29
Vinciguerria poweriae	47	36.66
Other Larvae	264	29.79
Hygophum benoiti	72	29.15
Labridae spp.	131	25.39
<u>Engraulis encrasicolus</u>	54	19.45
vinciguerria spp.	128	17.79
Vinciguerria attenuata	81	16.06
Vinciguerria nimbaria	51	11.86
<u>Sardinella aurita</u>	31	8.85
Sparidae spp.	78	5.55
Cyclothone braueri	271	5.26
Tunnidae	33	2.16

Tab 11.2.3. The main Larvae collection from 124 Station. Percentage (%) reported refers to the number of positive stations over the total number of stations performed.

11.3 Review of research on ichthyoplankton in Libyan waters

The species identification and spatial distribution of ichthyoplankton in the Libyan waters was investigated very little in the past. In the framework of the MedSudMed Project two multidisciplinary oceanographic surveys were designed also to carry out ichthyoplankton investigation in the western area of Libyan waters, between the Tunisian border and Musrata, and in the Gulf of Sirt, between Musrata and Bengazi.

The first survey, held in August 2006 allowed for the collection of fish larvae in 65 stations; 11 Orders, 39 Families, 39 Genera and 40 Species were identified during the sorting of samples. The most abundant species was anchovy, representing about 51% of the collected larvae and round sardinella with 9.6% of the larvae. Other species represented only a minor fraction except for Serranidae family (5.6%), the Gobidae family (3.7%), *Auxis rochei* (2.3%) and the Labridae family (3%) (Bonanno *et al.*, 2006). The second survey, in July 2008, allowed for the collection of larval specimens from 124 station in the Gulf of Sirt. 11 Orders, 32 Families, 38 Genera and 39 Species were identified (Table 11.2.3). The anchovy larvae (2.9%) and round sardinella larvae (1.6%) were not the predominant species. Each of the other species represented only a minor

fraction of the larvae collected, except for the genus Vinciguerria (16.3%), *Cyclothone braueri* (14.3%), the Gobidae family (9.5%) and the Labridae family (6.9%). The different results obtained in the two surveys are probably due to the geographical position of the areas, depth and width of continental shelf.

Historically no study on small pelagic fish species in Libyan waters has been carried out in the past. The only available information, based on sporadically collected specimens, concern mature fishes larger than 30 cm, collected by trawling and longline fisheries. Information in literature dates back to the XVIIII century with the classic work by Gunther on fish specimens in the collections of the British Museum in London (Cat.Fishes, vol.VIII, 1870), that mention (page 164) a specimen of Syngnathus agassizi, collected in Tripoli. The next information is given by Vinciguerra (1883), listing 11 fish species collected in the same area. Ninni in 1914 gives a complete list of 104 different fish species. Fage was the first one to record fish species from Eastern Libyan waters, collected by the Danish oceanographic Expedition (1908-1910); Vinciguerra gives a list of fish species caught in Benghazi. All these records are reviewed by Tortonese (1939), the author of the first truly scientific and modern publication about the ichthyofauna of Libya. He worked on the collections of the Natural History Museum of Tripoli, listing and describing 64 fish species. In his work among the speneans, the presence of the shark Carcharinus limbatus, is recorded as well as another 17 species that were new for the Libvan fauna (Contasemix, 1977).

The only publication referring to fishing conditions and catch composition in the area investigated during the cruises performed by the Romanian vessel "Delta Dunarii", comes from Gorgy *et al.* (1974). In the period August-September 1972, some data on small pelagics were gathered and reported after the survey at sea performed by a Japanese bottom trawler vessel "Hoyo Maru". The bottom trawl survey covered the Libyan waters and some other areas in the Southern Central Mediterranean. In the eastern part of the Gulf of Sirt and off Derna the report of the survey refers to an average catch/hour of 36 kg/hs, and composition of the catch dominated by sharks (37.5%), small fish (33.1%), common sea bream (8.2%), red mullet (5.8%) and silver hake (5.1%).

Other comparative source for fisheries data concerns the shelf area along the Tripolitania coast of Libya (Cherif 1966), is based on the cruise "Dauphin" (summer 1965). Contasemix (1977) published the only available information on the Icthyofauna of eastern coasts of Libya. Using active fishing methods (gill-nets, long line, hand lines) at day-time and night-time, 97 fish species belonging to 44 families and 12 orders were caught. Pelagic ichthyofuna was quantitatively poorly represented, consisting of only of 14 species belonging to 6 Families and 3 Orders. In the Gulf of Sirt similar information was made available by Instrupa (1975). In the western area, from the Tunisian border to Musrata, the data available are from the survey carried out by Sogerah (1977), and the last Survey in the Libyan coastal waters (Libfish; Lamboeuf, Reynolds, E. 1994; Lamboeuf, et al, 1995).

12. Sediments

The physical measurement and statistical treatment of grain-size data are basic tools in the investigation of marine sediments. Characterization of the size composition (granulometry) in a sediment sample can be measured either directly by separating each sediment component according to its physical size or indirectly taking into account the grain "hydraulic equivalents", which are based on the settling velocities of quartz spheres. In the following section the most common methods of grain-size determination are described.

12.1 Material and methods

Sieve Analyses, the oldest widely accepted method of grain-size determination, uses a nested set of sieves in which the size of the mesh is progressively smaller down the stack. The screen of each sieve is woven from brass or stainless steel wire to form square openings. Because of this geometry, the width of the intermediate axis is the critical determinant of grain size in sieved sediments. The sieves are agitated either mechanically or by hand, and each size class is trapped on the mesh that is too small for it to pass through. A nest of screens will, therefore, separate the sediment sample into groups of grains that range in size between the larger sieve through which they just passed and the sieve on which they were caught. The weight of each group (size class) is expressed as a percent of the total sample weight.

During the survey, sediment samples were collected with a box corer that keeps the vertical stratification of the sediments. Samples were collected at 11 stations set every 12 nm in the coastal area of Libyan waters . Part of the collected sediments were conserved in PVC tubes in order to maintain the vertical stratification, the other part was put in plastic bags to study granulometry and infauna. All samples were frozen for laboratory analysis. Moreover, prior to each station, a sismic analysis was performed with a Subbottom Profiler 3.5 kHz (Chirp), a system that gives information on the composition of the 1st layer of sediments and on the bottom morphology. Samples collected allowed for geochemical characterization of the most recent sediments (150-200 years), in view of describing the spatio-temporal variation of primary bio-productivity. The steps of the method used to process the samples are illustrated below.

a. Sediment classification

Prior to analysis, the frozen samples were left to thaw at room temperature. A 100g sub sample of sediment from each station was used for analysis. The sub sample was washed in freshwater in a large two litre beaker several times and finally in distilled water, to remove salt and debris of plants and animals. The sediment was left to settle on the bottom, then the clear water was decanted and the sediment was placed in a wide glass petri-dish and left to dry in an oven at 57°C for 24hrs. The Petri-dish was then taken out to cool. 100g of oven dried sediment was weighed and then placed on top of a nest of sieves secured on a mechanical sieve shaker (Octagon 200 Test Sieve Shaker) and agitated mechanically for 15 minutes. The test sieves used had mesh sizes 2.0, 1.0, 0.5, 0.250, 0.125, and 0.063 mm.

The sediment was removed from the sieves and any sediment stuck in the mesh was removed by mean of a soft camel-hair brush and added to the previous portion. Each fraction was then weighed to the nearest 0.01g and was expressed as a percent dry weight

of the initial sample. Cumulative percentages were plotted on probability paper. Sediments granulometry was espressed as Phi (\emptyset , -log₂(diameter)) after Krumbein (1934). Phi values of specific percentiles (16, 50, and 84%) were read and illustrated in specific plots as cumulative curves (Annex 2). Only those size classes from fine sands upwards are usually described by this curve except for those described in the preceding paragraph.

Measure of average size (Graphic mean, Mz): $M_z = \frac{\phi 16 + \phi 50 + \phi 84}{3}$

b. Sediments Organic Matter

In order to roughly measure sedimented organic matter, 10g of oven-dried sediment from each station was placed into a pre-weighted glazed porcelain crucible and ashed into a muffle furnace. The furnace was set at 600°C and was maintained at this temperature for one hour. After then the crucible was taken out of the furnace and covered with pre-weight aluminium foil and left to cool, then reweighed. The measure taken was the ash weight. Overall, the organic content was estimated as % dry weight = (dry weight – ash weight) *100 / dry wt.



Figure 12.1.1. Sampling with the box corer: PVC tubes and plastic bags.



No	Station	Longitude	Latitude	Collection method
1	M4	15°11.14'	35°29.70'	Box corer
2	M8	15°09.05'	33°59.69'	Box corer
3	M10	15°08.00'	33°14.69'	Box corer
4	L3013	32°41.44'	15°50.28'	Box corer
5	L3368	32°23.45'	16°28.61'	Box corer
6	L3751	31°34.28'	16°44.24'	Box corer
7	L4085	31°47.46'	17°45.27'	Box corer
8	L4418	31°29.46'	18°23.60'	Box corer
9	L4775	31°11.47'	19°01.93'	Box corer carota
10	L4760	32°03.43'	19°39.76'	Box corer
11	L4766M	31°43.04'	19°16.84'	Box corer

Table 12.1.1. Coordinates of the sampling sediment station of the MedSudMed-08 survey



Figure 12.1.3. 10g of oven dried sediment c. Carbonate Content



Figure 12.1.4: The furnace was set at 600°C

Carbonate Content was estimated using the most tried and proven method available: exposure of the remaining sediment (the following attack by H_2O_2 30 volumes) to HCl and H_2O_2 were used for the same weights of dry sediment.

12.2 Results and discussion

The main results of the 11 samples processed can be found in the different fractions of the sediments, Organic matter and CaCO₃ are shown in Table 12.2.1. Medium sand are generally found at depths > 150 meters. Medium sand are defined as having an average diameter of less than 20 microns in four stations and another 7 stations affine sand (see Folk Ward classification, 1974). Medium sands (1-2 Phi) and fine sand (1-3 Phi) can be exceptionally rich when they exist as thin layers on rocks breaking through or close to the sea-bed, always have a carbonate content of between 52 and 92% but medium sand is less in carbonates (33-62%).

In the arid or sub-arid nature of the coastal regions, the extent to which sand-dunes are developed and the existence of frequent violent southerly winds are main driving factors for living communities. The impact that such features may have on coastal areas was not investigated. In this study a description of the sediment granulometry along coastal Libyan waters was provided. Based on the data gathered, further studies are ongoing to detect the sea area which is affected by southerly winds and other related phenomena.

Station	Gravel %	Sand %	Mud Clay %	Graphic Mean (Mz)	Sediment classification	% Organic matter	% CaCO ₃
4M	0.0	93.6	6.2	1.5	medium sand	1.7106	45.24
M8	9.2	90.6	< 0.1	1.5	medium sand	0.8944	32.45
M10	16.1	83.5	0.2	1.3	medium sand	0.9288	50.50
L 3013	1.5	95.6	2.8	2.2	fine sand	1.2906	84.17
L 3368	0.5	89.7	9.6	2.3	fine sand	1.1710	52.86
L3751	3.6	88.1	8.2	1.8	medium sand	1.4047	62.83
L 4085	0.6	93.8	5.6	2.4	fine sand	1.0303	83.16
L 4418	2.9	93.3	3.6	2.2	fine sand	1.3267	78.20
L 4775	4.2	88.1	7.5	2.0	fine sand	1.1526	81.65
L 4760	11.4	73.3	15.1	2.4	fine sand	0.7846	74.39
L 4766M	1.8	89.3	8.7	2.1	fine sand	4.7744	92.12

Table 12.2.1. Sediment samples composition in terms of organic matter and CaCO₃.

13. Notes, recommendations and acknowledgments

The survey was conducted in cooperation with several institutes. MBRC scientists on board the vessel were involved in the work shifts and participated in the discussions on sampling design wherever changes had to be made. Moreover, the survey was an occasion to increase the technical skills of those who had limited experience in this type of field work. As mentioned above, a set of samples was sent to the MBRC during the survey and at the end of the survey a copy of electronic data was given to the Libyan focal point (CTD, acoustics, ADCP, base maps, coordinates of the stations, navigation data). The remaining information, such as the results of samples analysis for nutrients, heavy metals and trace elements, will be sent to the MBRC as soon as they become available.

The survey was conducted successfully. The decisions regarding the operations to be conducted on board were made in agreement with the MBRC staff who were involved in all stages of the data collection, sampling conservation and analysis. No particular problem was encountered during the survey, which allowed for smooth performance of the work and rigorous data collection.

As agreed prior to the survey, the follow-up to the work carried out so far will consist in the organization of training courses for the processing of the data and samples collected. The processing will be carried out in collaboration with the institutes that participated in the survey and will be organized in cooperation with the MBRC.

Captain Emanuele Gentile and all his crew are gratefully acknowledged for their willing participation and the interest they showed in the scientific survey "MedSudMed-08". It is important to underline the high professional level and readiness of the R/V Urania crew who participated in all the activities in synergy with the scientists. All the crew showed great willingness and flexibility, allowing the scientists to conduct activities in secure conditions and to overcome unexpected events.

Lastly, the particular sensitivity and helpfulness of the whole crew with the scientists of the MBRC and the Libyan coast guard needs to be underlined and acknowledged.

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Distribution maps of the larvae identified

Figure 5.1. Number of anchovy (Engraulis encrasicolus) larvae (from 1 to 6 specimens).



Figure 5.2. Number of sardinella (Sardinella aurita) larvae (from 1 to 19 specimens).



Figure 5.3. Number of Gobidae larvae (from 1 to 19 specimens).



Figure 5.4. Number of Callionymus maculates (only 1 specimen).



Figure 5.5. Number of Triglidae larvae (only 1 specimen).



Figure 5.6. Number of Tunnidae larvae (from 1 to 7 specimens).



Figure 5.7. Number of Sparidae larvae (from 1 to 11 specimens).



Figure 5.8. Number of Labridae larvae (from 1 to 50 specimens).


Figure 5.9. Number of Serranidae larvae (from 1 to 4 specimens).



Figure 5.10. Number of Carangidae larvae (from 1 to 4 specimens) ...



Figure 5.11. Number of Trachurus spp. Larvae (only 1 specimen).



Figure 5.12. Number of *Scorpaena scrofa* larvae (only 1 or 2 specimens).



Figure 5.13. Number of Vinciguerria attenuata larvae (from 1 to 17 specimens).



Figure 5.14. Number of Vinciguerria nimbaria larvae (from 1 to 7 specimens).



Figure 5.15. Number of Vinciguerria poweriae larvae (from 1 to 11 specimens).



Figure 5.16. Number of Vinciguerria spp larvae (from 1 to 20 specimens).



Figure 5.17. Number of *Electrona rissoi* larvae (from 1 to 12 specimens).



Figure 5.18. Number of Hygophum benoiti larvae (from 1 to 15 specimens).

Results of granulometric analysis







Cumulative curve (%)



Cumulative curve (%)





— Cumulative curve (%)



L3368





Cumulative curve (%)



Cumulative curve (%)



Cumulative curve (%)









L4775





CTD Profiles for each station of the "MedSudMed-08" Oceanographic Survey




































































Analysis of nutrients



Figure 6.1.1. Map of the stations. Blue circles show the location of nutrient samples. Blue, green and red boxes show the location of samples for the determination of trace metals and stable nitrogen and carbon isotopic composition of POM.



Figure 6.2.1. AutoAnalyzer III (Continuos Flow) Bran+Luebbe

Nutrient	mM ,Detection limit	mM ,Precision
NO3+NO2	0.01	0.003
NITRITE	0.01	0.003
PHOSPHATE	0.010	0.005
SILICATE	0.05	0.01

 Table 6.2.1 Precision and detection limits of nutrients



36°N

34°N

32°N

36°N

34°N

32°N

36°

34°N

32°N

36°

34°N

32°N

Figure 6.3.2. Horizontal Nitrate (NO3) distribution from top (0m) to 400m.

0.3

0.2

0.3

0.2



Figure 6.3.3. Horizontal Phophate (PO4) distribution from top (0m) to 400m.



Si-Si(OH)4 [umoli/I] @ Depth [m]=7!



Si-Si(OH)4 [umoli/I] @ Depth [m]=50

36°N 34°N 32°N



Figure 6.3.4. Horizontal Silicate (Si(OH)4) distribution from top (0m) to 400m.



Figure 6.3.5: Horizontal Ammonium (NH4) distribution from top (0m) to 300m.



Figure 6.3.6.Vertical nutrient distribution, fluorescence and salinity profiles along a transect from the coast to an off-shore station in the Gulf of Sirte (immage below to the left).

1.75

1.5

1.25



Figure 6.3.7: Vertical nutrient distribution and salinity profile along a transect located in the middle of the Gulf of Sirte.



Figure **6.3.8.** Vertical nutrient distribution along a transect from coast to off shore in the Gulf of Sirte.



Figure 6.3.9. Vertical nutrient distribution along the transect from the Sicilian coast to the Libyan coast.

Annex 5

Analysis of trace metals



Figure 7.1.1 Location map of samples collected for trace metal analyses. Blue squares show the location of samples where trace metals were measured.



Figure 7.2.1. Distribution patterns of Mo (nmol/l) vs depth.



Figure 7.2.2. Distribution patterns of Cu (nmol/l) vs depth.



Figure 7.2.3. Distribution patterns of Ni (nmol/l) vs depth.



Figure 7.2.4. Distribution patterns of V (nmol/l) vs depth.



Figure 7.2.5. Distribution patterns of Co (nmol/l) vs depth.



Figure 7.2.6. Distribution patterns of Cd (nmol/l) vs depth.



Figure 7.2.7. Distribution patterns of Pb (nmol/l) vs depth.



Figure 7.3.1. Vertical section of nickel concentrations along the Sicily-Libya transect



Figure 7.3.2. Vertical section of Ni concentrations along the Sicily-Libya transect.



Figure 7.3.3. Vertical section of Cd concentrations along the Sicily-Libya transect.



Figure 7.3.4. Vertical section of Pb concentrations along the Sicily-Libya transect.



Figure 7.3.5. Vertical section of Mo and V concentrations along the Sicily-Libya transect.



Figure 7.3.6. Vertical section of Co concentrations along the Sicily-Libya transect.

Annex 6



Carbon and Nitrogen Isotopes in Particulate Organic Matter (POM)

Figure 9.2.1 $\delta^{15}PON$ vs. depth at M1, M3 and M6 stations



Figure 9.2.2 $\delta^{15}PON$ vs. depth at M1, M3 and M6 stations



Figure 9.2.3 $\,\delta^{15}PON$ values vs. depth in four stations of the Gulf of Sirte.



Figure 9.2.4 Latitude distribution of δ^{15} N-PON at: a) upper 200m and b) below 200m in the transect and Gulf of Sirte.



Figure 9.2.5 Longitudinal distribution of δ^{13} C-POC in the: c. upper 200m and d. lower than 200m in the transect and Gulf of Sirte



Figure 9.2.6 Distribution of δ^{13} C and δ^{15} N POM values with respect to different stations (near cities, transect and far from cities)





Figure 9.2.6. Particulate $\delta^{13}C$ vs temperature in a) transect; b) Gulf of Sirte and particulate $\delta^{15}N$ vs temperature in c) transect; d) Gulf of Sirte



Figure 9.2.7. Distribution of $\delta^{13}C$ values vs. depth

Beneficiary countries

Countries with waters included in the GFCM Geographical Sub-Area (GSAs) 12-16 and 21. Libya, Malta, Italy and Tunisia.

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